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DECEMBER 1956

QUARTZ-COESITE STABILITY RELATIONS AT HIGH TEMPERATURES AND PRESSURES*

GORDON J. F. MacDONALD

ABSTRACT. Coesite-quartz stability relations have been investigated using the "simple squeezer" high-pressure apparatus. Samples of amorphous SiO_2 in the form of silicic acid ($SiO_2 \cdot nH_2O$) were subjected to pressures up to 80,000 bars and temperatures from 400-800°C. The equation of the curve separating the fields of quartz and coesite is $P = 22.5\ T + 9500$ where P is in bars and T is in degrees Centigrade with coesite stable in the high-pressure region. The only phases produced were quartz and coesite. The equilibrium curve plus estimated thermal gradient in the Earth indicate that quartz should invert to coesite at a depth between 60 and 100 kilometers within the Earth.

The entropy of coesite at 25°C and one bar is 8.6 ± 0.7 cal/deg.mole as determined by the equilibrium curve. The heat of transition of quartz to coesite is −225 ± 150 cal/mole. The thermal data on coesite indicate that the approximate maximum depths within the Earth at which fayalite and forsterite are stable relative to "FeO" and MgO plus coesite are 200 and 1100 km.

INTRODUCTION

Coes (1953), in the first announcement of the very important high-pressure work carried on at the Norton Company, Worcester, Massachusetts, describes the synthesis of a new high-pressure polymorph of SiO_2. The new polymorph is characterized by a density of 3.01, 13.6 percent denser than quartz. Sosman (1954) proposed that the new polymorph be called coesite. Since this polymorph has not as yet been found in nature, Sosman also suggested the alternative name "Silica C." In the present paper the new polymorph will be called coesite.

Coes synthesized coesite at pressures near 35,000 bars in the temperature range 500-800°C from various mixes. At temperatures above 800°C and at about 35,000 bars quartz formed from the mixes rather than coesite. This result was then the first indication of the position of the equilibrium curve between coesite and quartz. Griggs, Kennedy, and Fyfe (1955) in the course of investigating various reactions at high pressures, synthesized coesite at lower pressure and temperatures than those reported by Coes. Because of the geologic importance of quartz, it was thought desirable to obtain in greater detail the equilibrium curve between coesite and quartz. This curve would fix the maximum pressures at which quartz could form and, together with the temperature gradient in the Earth, would fix the maximum depth within the Earth at which quartz would be stable.

The problem of the quartz-coesite equilibrium is part of the more general problem of the stability of minerals having a loosely packed framework structure. Minerals with such framework structures (feldspars, feldspathoids,

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quartz, etc.) make up a major portion of the rocks exposed at or near the Earth's surface. An important question is: to what maximum depth within the Earth are such minerals stable? It appears very probable that high density phases having compositions of these framework minerals are stable at moderate depths within the Earth. Robertson, Birch, and MacDonald (in press) have shown that nepheline plus albite might be expected to convert to the denser phase, jadeite, at depths of approximately 10 to 40 km within the Earth. Pure albite would invert to jadeite plus quartz at somewhat greater depths. Since alkali feldspar plus quartz are the dominant constituents of granites and granodiorites, it might be possible to have a rock equivalent in composition to a granite, but made up of denser, less compressible phases at a moderate depth within the Earth. The depth at which such a rock would be stable would depend on the position of the quartz-coesite equilibrium curve as well as on the position of the breakdown curves for the alkali feldspars, and of the temperature gradient.

The present study is concerned with the direct experimental determination of the quartz-coesite equilibrium relations. Silicic acid ($SiO_2 \cdot nH_2O$) and quartz have been converted to coesite at high pressures. From the position of the equilibrium curve and the thermodynamic properties of quartz, approximate thermodynamic properties of coesite have been obtained. These properties allow an estimate of the upper pressure limit of stability of such minerals as olivine and pyroxene, long considered the dominant constituents of the Earth's mantle.

EXPERIMENTAL DETAILS

The experimental work was carried out on the "simple squeezer" high-pressure apparatus designed by Professors Griggs and Kennedy and described by Griggs, Kennedy, and Fyfe (1955). Since this high-pressure system is being described in detail by Griggs and Kennedy elsewhere, only the basic features of the apparatus need be mentioned here. The confining pressure is produced by pressing two pistons together. The piston faces that come in contact across the specimen have a diameter of ¼ inch. The sample is placed between the piston faces and is separated from each face by a layer of platinum-10% rhodium foil. The pistons are pressed together by a commercial hydraulic jack, supported by a framework of plates and tie rods. The sample is heated by an external furnace enclosing the pistons and sample. The temperature is measured by a chromel-alumel thermocouple placed in a hole in one of the pistons. The tip of the thermocouple is about ¼ inch from the sample.

In the simple squeezer the pressure is n .irectly measured but is calculated from the force applied to the confining pistons. The sample between the pistons may not be under a hydrostatic pressure, and the strain energy resulting from shearing the sample might affect the position of the equilibrium curve. There is an uncertainty in the pressure acting on the sample and an uncertainty in the effect of shear on equilibrium relations. An attempt to evaluate these uncertainties has been made (MacDonald, in press). The calcite-aragonite equilibrium curve was determined, using the simple squeezer,

and the results were compared with those of Jamieson (1953) derived from thermochemical considerations. The simple squeezer gave an equilibrium curve about 1500 bars lower in pressure at 10,000 bars than the curve obtained by Jamieson. The reasons for this discrepancy are as yet uncertain but they do indicate perhaps that pressures calculated for the simple squeezer may be uncertain by as much as 15 percent.

The starting material in all but a few exploratory runs was Mallinckrodt silicic acid, $SiO_2 \cdot nH_2O$. Various other materials were tried but none gave as good reaction times as $SiO_2 \cdot nH_2O$. As an illustration of this, quartz at 580° and 30,000 bars showed about 10 percent conversion to coesite in a one-hour run. Silicic acid showed 100 percent conversion to coesite. Various mixtures of alkali silicates were also tried but not used because of the appearance of phases other than quartz and coesite. Using $SiO_2 \cdot nH_2O$, the only phases observed either optically or by X-ray were quartz and coesite.

The products were identified by comparing the X-ray patterns obtained on a Norelco high angle diffractometer with a standard quartz pattern and with the X-ray spacings of coesite given by Coes (1953). The pattern of coesite is quite distinctive, and there is no chance of confusing the pattern with that of other phases of SiO_2. The products were also examined optically. Since coesite has a mean index of refraction of 1.60, it is readily distinguishable from quartz, and small amounts of coesite can be detected.

The sample to be exposed to high pressures is placed on the platinum-10% rhodium foil in the form of a dry powder or admixed with a drop of water to form a paste. The presence of water does not appear to affect either the position of the equilibrium curve or the rate at which equilibrium is attained. An original thickness of powder of 0.02-0.03 inch results in a wafer about .005 inch thick in the center. The wafer is generally transparent, though in some cases milky in appearance.

The sample is first heated to the desired temperature and then the pressure is raised. The time required to bring the sample to temperature varied from 15 to 30 minutes. The application of pressure took only a few seconds. The order of raising the temperature and pressure is important. By first raising the temperature and then the pressure, the sample is at a high pressure only at the desired temperature. The high-pressure form, coesite, can form only at the required temperature and not at some lower temperature. After the sample is held at the required conditions of temperature and pressure for a suitable time, ranging from one to 24 hours, depending on the conditions of the experiment, the sample is quenched by releasing the pressure and placing the sample in water. In this way temperature and pressure are reduced to room values in about 5 seconds. This quenching assures that coesite formed at high pressures is not converted to quartz in the process of cooling the sample.

RESULTS

The results of 43 runs are summarized in table 1. This table lists the temperature and pressure conditions of the experiment and results from X-ray

and optical examination of the products. Almost all the runs were made in the temperature range 400-600°C. The lower limit in temperature was set by the rate of reaction. At 350°C runs of 24 hours did not produce coesite even though the runs were well inside the coesite field. At 400°C coesite formed in 24 hours or less. The upper limit in temperature of 600°C was set by the use of high-speed steel pistons. These pistons do not deform appreciably at temperatures below 600°C and pressures below 30,000 bars but do deform rapidly at higher temperatures. One important run at 815° and 31,000 bars was made using Kentanium pistons. This experiment, as well as three other runs at pressures about 50,000 bars, were made in collaboration with Professor David T. Griggs.

The length of time the sample was held at the required temperature and pressure depended on the temperature of the run. The runs at 400°C were maintained at temperature and pressure for 10-24 hours, whereas runs near 600°C were only about an hour in duration. In this fashion an attempt was made to achieve at least partial equilibrium at all temperatures. Repeat runs of increased duration were made near the boundary curve. A run at 480°C and 20,000 bars for one hour produced only quartz. Since this run is near the boundary, it was repeated and held at pressure for 20 hours. The longer run again produced only quartz. Similarly, runs of one hour at 500°C and 22,000 bars produced coesite, while an 8-hour run at 500°C and 20,000 bars produced only quartz.

The points that were used to determine the equilibrium curve are shown in figure 1. Only those points near the curve are plotted. The solid black squares indicate runs in which coesite was formed. Strictly speaking, the boundary line is a line separating runs in which a small amount of coesite formed from runs in which no coesite formed at all. The results of the runs are consistent, and repeat runs of longer duration do not alter this boundary. For these reasons the boundary curve is thought to represent the equilibrium curve. In order to demonstrate that this curve is actually the equilibrium curve, a detailed study should be made using coesite as a starting material and showing that coesite converts to quartz at pressures lower than those given by the curve in figure 1. In the present study insufficient coesite was made to carry out such a program.

The size of the squares in figure 1 is approximately proportional to the estimated uncertainty in the conditions of the individual run. The uncertainty in temperature is estimated to be about $\pm$ 10°C, due to the difficulty in placing the thermocouple in the identical position relative to the sample in every run. The pressure uncertainty in any given run is estimated to be $\pm$ 500 bars, due to the scale of the pressure gauge on the jack and small changes in pressure during a run resulting from fluctuations in room temperature. This estimate of the uncertainty assumes that the total force acting on the piston gives a good measure of the pressure and that in addition the pressure is uniform over the entire sample.

The equation representing the equilibrium line is $P = 22.5(\pm 8)\ T + 9500(\pm 4000)$, where T is in degrees Centigrade and P is in bars. The estimated uncertainties are derived by examining possible curves that could be

TABLE 1

Results of Subjecting $SiO_2 \cdot nH_2O$ to High Temperatures and Pressures

Temperature °C	Pressure bars	Time hrs	Results of X-ray and optical examination of materials
382	62,000	1.5	coesite
390	83,000	1.5	coesite
396	28,000	16	coesite and minor quartz
400	17,500	22	quartz
408	19,500	14	minor coesite and quartz
414	18,000	10	quartz
432	16,000	13	quartz
440	18,000	2	quartz
440	18,000	11	quartz
442	20,000	12	coesite and quartz
454	18,000	1	quartz
475	21,000	1	quartz
480	20,000	2	quartz
480	20,000	20	quartz
485	56,000	1	coesite
490	18,000	1	quartz
492	16,000	1	quartz
493	16,000	24	quartz
500	19,000	18	quartz
500	20,000	2	quartz
500	20,000	8	quartz
500	22,000	1	minor coesite and quartz
500	23,000	1	coesite and quartz
500	30,000	10	coesite
504	19,000	2	quartz
524	21,000	1	minor coesite and quartz
530	24,000	1	coesite and quartz
536	22,000	1	quartz
540	22,000	1	quartz
540	23,000	1	minor coesite and quartz
550	19,000	1	quartz
550	20,000	1	quartz
550	21,000	6	quartz
554	25,000	4	coesite and quartz
560	23,000	1	minor coesite and quartz
573	24,000	1	coesite and quartz
576	23,000	1	quartz
580	22,000	6	quartz
580	30,000	1	coesite
582	22,000	1	quartz
584	26,000	1	coesite and quartz
590	24,000	1	minor coesite and quartz
815	31,000	1	minor coesite and quartz

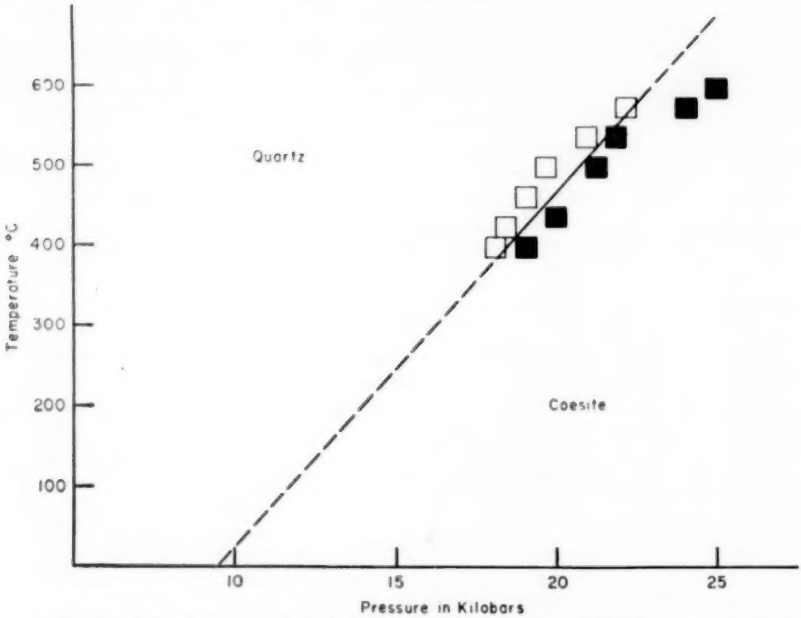

Fig. 1. Plot of runs used in determining quartz-coesite equilibrium curve. Size of square is approximately proportional to estimated uncertainty in the temperature and pressure of the run. One square may represent two or more runs. (See table 1.)

drawn without contradicting the experimental determinations, taking into account the uncertainty in the individual points. The major reason for the large uncertainties is that the temperature interval in which the reaction has been studied is only 200°C. The run at 815°C and 31,000 bars reduced this uncertainty somewhat, but more measurements are needed at high temperatures and pressures.

OTHER POSSIBLE HIGH-PRESSURE POLYMORPHS OF SiO_2

Three runs were made at pressures greater than 50,000 bars in order to investigate possible higher-pressure forms of SiO_2. A run at about 83,000 bars and 390°C produced only coesite. The run was only an hour and a half long, so that equilibrium may not have been reached at this low a temperature. It is considered very probable that a series of higher density forms of SiO_2 can be synthesized. It is most improbable that coesite is the form of SiO_2 having a rutile type of structure with silicon in six coordination, as suggested by Thompson (Birch, 1952, p. 234). Such a form should have a density of roughly 4.5 to 5.0. Since coesite has a density of only 3.0, a number of intermediate forms of SiO_2 are possible before a rutile-like form of SiO_2 is reached at extreme pressures.

THERMODYNAMIC DATA ON COESITE

The slope of the curve of univariant equilibrium shown in figure 1 and the intersection of the curve with the zero pressure axis, together with thermodynamic data on quartz, allow an estimate of the entropy and heat of formation of coesite. The slope of the curve determines the entropy of coesite, provided the difference in volume between cosite and quartz is known, since $dP/dT = \frac{\Delta S}{\Delta V}$. The density of coesite is 3.01 as reported by Coes (1953) and Ramsdell (1955). Using this density and the density of quartz, the volume change for the transition

$$\text{quartz} = \text{coesite}$$

is given by $\Delta V = -2.71 \pm 0.1$ cc/mole. The determined slope of the curve is 22.5 ± 8 bars/degree, which leads to a value of the change in entropy for the transition of $\Delta S = -1.4 \pm 0.6$ cal/deg.mole. Since quartz has an entropy at 25°C and 1 bar of 10.0 cal/deg.mole (Kelley, 1950), coesite has an entropy of 8.6 ± 0.7 cal/deg.mole at 25°C and 1 bar. In this calculation of the entropy it is assumed that the difference in compressibility of quartz and coesite is less than 1×10^{-5} bars^{-1} and that the difference in thermal expansion is less than 1×10^{-4} degrees^{-1}, since the entropy change is strictly valid only at 10,000 bars and should be corrected for the change of entropy with pressure. This change is probably considerably smaller than the uncertainties introduced by the uncertainty in slope of the transition curve. Furthermore it is assumed that the transition curve is a straight line, since the experiments are not of sufficient accuracy to detect any curvature.

The heat of transition for the reaction at 25°C and 1 bar is determined by the intersection of the transition curve with the 25° axis, provided that ΔV for the reaction is assumed constant, and the change of entropy for the reaction is known. Using an entropy change of -1.4 ± 0.6 cal/deg.mole and an intersection of $10{,}000 \pm 4000$ bars, a heat of transition of -225 ± 150 cal/mole is obtained.

TABLE 2

Thermochemical Data on Quartz and Coesite

	V cc/mole	S cal/deg.mole	ΔH_f cal/mole
quartz	22.64	10.0 ± 0.1	0
coesite	19.93 ± 0.1	8.6 ± 0.7	-225 ± 150

POSSIBLE NATURAL COESITE

Coesite has not as yet been found in nature. The stability curve and estimated temperature gradients within the Earth (Birch, 1955) indicate that quartz should convert to coesite at a depth between 60 and 100 kilometers within the Earth. This indicates that any rock containing excess SiO_2 and originating at 100 km within the Earth should contain coesite, provided the rock had not subsequently undergone thermal metamorphism. In addition, the quartz-coesite boundary lies some 20 to 30 km above the graphite-diamond

transition boundary within the Earth (MacDonald, ms.), so that any rock in which diamonds crystallized should contain coesite, provided the rock were oversaturated with respect to SiO_2. The eclogite inclusions found within the kimberlite pipes of South Africa might contain coesite, since they contain diamonds, but most of the eclogites are undersaturated with respect to SiO_2.

A preliminary search of thin sections of eclogite samples from South Africa, Austria, and Norway has disclosed no coesite. The search for coesite in rocks is made difficult by the fact that the optical properties of coesite are nearly identical with those of apatite.[1]

O. F. Tuttle, at the New Orleans meeting of the Geological Society, made the very interesting suggestion that lamellae found in quartz grains in strongly deformed rocks might represent planes along which quartz has converted to coesite. The lamellae could then be interpreted in terms of a shear transformation in which the sheared region contains a new phase, coesite, and the boundary of the lamellae with the quartz is a phase boundary. The quartz lamellae are a possible natural source of coesite that should be investigated.

COESITE AND THE STABILITY OF OLIVINES AND PYROXENES AT DEPTH

The thermochemical data on coesite can be used to obtain a rough estimate of the maximum depth within the Earth at which these minerals are stable. Transitions of the form

$$Mg_2SiO_4 = 2MgO + SiO_2 \,|_{\text{coesite}} \qquad \Delta V = -1.4 \text{ cc}$$

$$Fe_2SiO_4 = 2''FeO'' + SiO_2 \,|_{\text{coesite}} \qquad \Delta V = -5.3 \text{ cc}$$

show a negative volume change, since the mixture of the oxide and coesite has a lower volume than the corresponding olivine. At some high pressure the mixture of the oxides should become stable relative to the olivine, provided that no intervening high-pressure forms of olivine occur. Using the data on coesite and thermochemical data on the olivines and oxides (MacDonald, ms.), it is found that forsterite would break down to the oxides at a pressure of about 450,000 bars, while fayalite would break down at about 60,000 bars,[2] assuming the temperature to be on the order of 1000-2000°C. These conditions would correspond to a range of depths of 200-1100 km within the Earth. The mineral olivine is then probably unstable relative to the oxides at depths in the Earth below 1100 km. These calculations assume that no new phase of olivine appears with a density less than the density of the oxides and coesite, and

[1] Professor Harold Fairbairn has looked for coesite in eclogite. He reports: "An attempt to find coesite in an eclogite inclusion in kimberlite (Roberts Victor Mine, Transvaal) was unsuccessful. A 340 gm sample was separated into sized fractions. A −400 screen fraction weighing 80 gm was decomposed by HF, and heated successively in HCl and H_2SO_4. The small remaining residue all floated in bromoform (D = 2.9), indicating no coesite (D = 3.01). Coarser fractions were treated with heavy liquids and passed through a Frantz separator. A small non-magnetic residue of density between 2.9 and 3.1 likewise failed to show any coesite."

[2] A single experiment was made to test this conclusion in which synthetic fayalite provided by Professor Kennedy was held at 480°C and 56,000 bars for one hour. No change was observed in the fayalite. The experiment is not considered conclusive since the run was only one hour long and equilibrium may not have been attained at this low temperature.

furthermore that no denser phases of FeO, MgO, and SiO_2 appear. The limits proposed above are then maximum limits; the appearance of still denser forms would lower the pressure needed to transform olivine. Similar calculations on pyroxenes indicate that the pyroxenes would also break down at comparable depths. The calculations are very approximate because of the high temperatures and pressures involved and the uncertainty of the compressibility and thermal expansion of the phases under these conditions. It is of interest to note that the range from 200 to 1100 km within the Earth includes the region (200-900 km) suggested by Birch (1952) as a region in which there is a gradual shift toward high-pressure modification of ferromagnesian silicates.

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Professors George C. Kennedy and Harold Fairbairn critically reviewed the manuscript, and their suggestions did much to improve the presentation.

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A SIMPLE APPARATUS FOR HIGH PRESSURES AND TEMPERATURES*

D. T. GRIGGS and G. C. KENNEDY

ABSTRACT. A simple apparatus, based on the principle of Bridgman's shearing apparatus, provides pressures of 80 kilobars at 500°C, 50 kb at 800°C, and 20 kb at 1000°C. Pressure is known within approximately 5 percent, and temperature to 5°C. The sample, in powdered form, is compressed between two pistons which are externally heated and pressed together by a hydraulic jack. Under certain circumstances water vapor pressure in the sample may equal total pressure, even at high temperatures. The apparatus is extremely easy to use, and equilibrium seems to be attained more rapidly than in the case of pure hydrostatic pressure. Thus, it seems well adapted for study of metamorphic reactions within the range of pressure and temperature to be expected normally in the outer 50-100 kilometers of the Earth.

INTRODUCTION

Bridgman (1935) was the first to make quantitative experiments on a sample compressed between two flat piston faces. He showed theoretically (1937) that, to a first approximation, the stress system in such a compressed disk is hydrostatic except for a thin peripheral region (less than 5 percent of the radius in general). Hence the pressure over most of the sample is approximately equal to the force with which the pistons are pressed together, divided by the area of the piston face. Bridgman (1952, p. 177) later demonstrated that the pressure so calculated is equal to the actual pressure within "a few per cent" which was within the experimental error. This was done by measuring the electrical resistance of bismuth in an apparatus of this type. Its resistance changes sharply when bismuth undergoes a polymorphic transition at 24.9 kilobars at room temperature. The pressure at which this transition occurs had been previously determined by Bridgman in a conventional hydrostatic apparatus.

Larsen and Bridgman (1938) attempted to bring about mineral transitions in the shearing apparatus but encountered little success, as work was performed at room temperature. Griggs (1941) used apparatus of this type in experiments on metamorphic reactions at low pressures and moderate temperatures and had recently been using such an apparatus for experiments at 100 kb, room temperature. Kennedy suggested that the Bridgman apparatus might be adapted in such a way that mineral reactions might be explored at high temperatures and pressures and that water vapor might be retained. Hence, this cooperative project was undertaken. Experiments were started with a press on hand and pistons which had been acquired for work at room temperature, 100 kb. Later, apparatus more suitable to the purpose was constructed. The latest apparatus, familiarly known as the "simple squeezer," is described here.

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DESCRIPTION OF APPARATUS

The apparatus is shown in plate 1, and schematically in figure 1. A Blackhawk 20-ton ram pushes the pistons together in a homemade press. The ram is activated by a hand pump through a manifold valve which allows operation of five presses simultaneously. Each ram is fitted with a U. S. Gauge Company 10,000 lbs/in^2 gauge. A 700 bar Heise gauge is connected to the manifold valve and is used to check these gauges. Rudimentary measures are taken to provide coaxial alignment of the pistons. Alignment has not been found to be critical, fortunately, since thermal distortions make exact alignment very difficult.

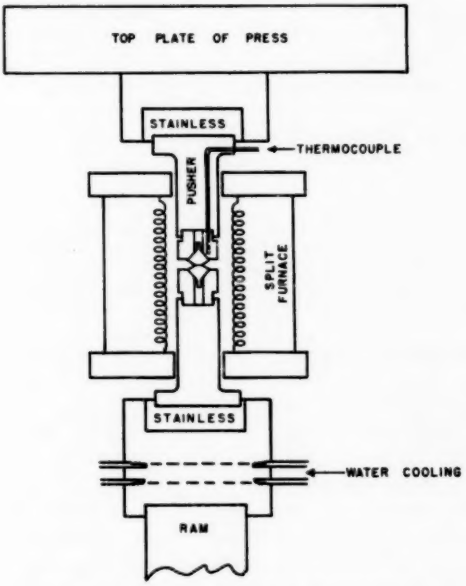


Fig. 1. Schematic drawing of apparatus.

The pistons, holders, and pushers are heated by a Hevi duty Electric Company split furnace type 123-1 of 400 watts capacity. This furnace is run over-voltage for temperatures above 700°C by means of a variable transformer. Temperature is controlled by a Brown Pyrovane controller, operated by a thermocouple inserted in the furnace winding, to respond to heater element temperature.

Materials with the highest compressive strength are most desirable for the pistons. Such materials are brittle and must be subjected to confining pressure to prevent brittle fracture. This confining pressure is provided by making the pistons conical as shown in figure 2. Two cone angles have been used: 20°, and 45° half-angle. Neglecting friction, the normal stress on the cone surface is given by the force divided by the area of the cone surface

projected on a plane normal to the force. For .250″ diameter piston faces in the designs illustrated, the normal stress is 29 percent of the sample pressure in both cases. The radial stress, normal to the applied force, is 27 percent and 20 percent of the sample pressure for the 20° and 45° cones, respectively. Higher confining pressures are desirable to achieve the highest sample pressures but have so far not been attained, due to insufficient strength in the material of the holders. Lubrication on the cone surface is provided by a thin copper foil, which has small strength at elevated temperatures. Even at 1000°C, this foil does not entirely squeeze out.

Fig. 2. Pistons and holders: A. 20° cone, used only for cemented carbides. B. 45° cone in configuration used for high speed and stellite pistons. When using this cone angle for carbides, the upper and lower cylindrical sections are omitted, and the acute angle between the two cones is flush with the top of the holder. In both cases, .003″ copper sheet was placed between the pistons and holders to serve as lubricant.

The highest pressures have been attained with cemented carbide pistons in the 20° cone shape (fig. 3). Kennametal grade K-6 was used to 800°C, where oxidation became excessive. Kentanium K-161B was used from 800°C to 1000°C. In these experiments, Carpenter 883 steel was used for holders to 500°C, and Inconel X from 500° to 1000°C. Due to the decrease of strength of the Inconel at high temperatures, the area of the piston face had to be diminished with successively higher pressures to prevent excessive deformation of the Inconel. At 1000°C, the diameter of the piston face was 0.10″ for sample pressures of 21 kb. The normal stress on the cone face was only 4 percent of the sample pressure, or about 0.8 kb. With Stellite 98M2 holders, it is anticipated that .250″ diameter piston faces could be used to 1000°C and that the sample pressures attained would be somewhat higher than those shown in figure 3, due to the beneficial effect of larger confining pressure.

Stellite 98M2 has been used in pistons with 45° cone (fig. 2). The pressures attained with these pistons is about 60 percent of that attained with the carbide pistons (fig. 3). The stellite 98M2 pistons have the advantage, however, of being less brittle than the carbide pistons and hence less subject to cracking.

All types of pistons, but most particularly cemented carbide, develop fractures long before their useful life is over. These fractures are typically of two types: (1) radial fractures extending up to but not entering the flat face; (2) spalling fractures roughly parallel to the upper, unsupported conical surface. In the case of carbide pistons, the former type of fractures almost

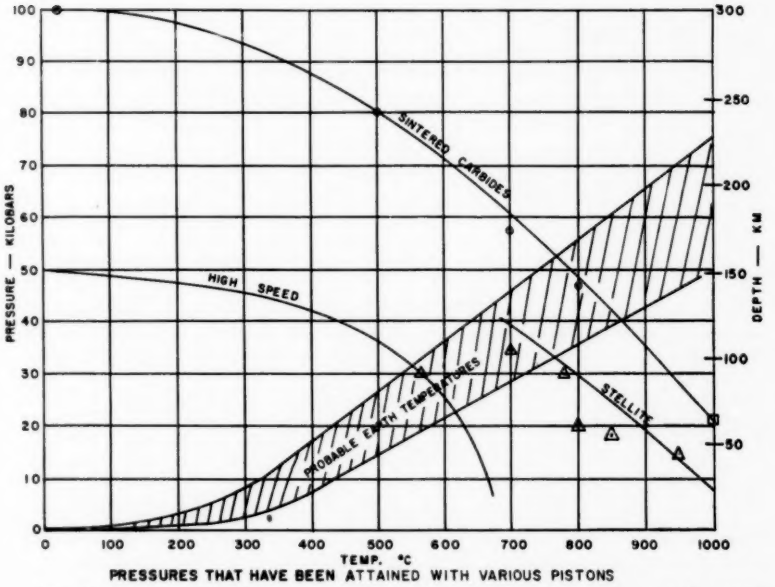


Fig. 3. Maximum working pressures that have been attained. In many of the points, no piston damage was observed. The Earth temperatures correspond to a surface heat flow of 1.2 x 10^{-6} cal/cm^{2}sec, 2/3 to 3/4 originating in a 30 km crust, and a conductivity in the mantle of .008 cal/cm sec deg.

invariably appears after any run at 50-60 percent of the maximum pressure to which the pistons are usable. They are initially very fine radial cracks, and after repeated runs at higher pressures they gradually widen. Destructive fracture in carbide pistons of the type shown in figure 2-A occurs after very appreciable plastic flow has occurred and may occur in a test at considerably lower pressure than the piston has already withstood. Such fracture most commonly takes the form of shear on an inverted 45° cone, passing through the outer boundary of the piston face. This shear is typically associated with radial cracks external to the cone, and occasionally with spalls.

Stellite and High Speed Steel have much less tendency to crack and frequently their life is terminated simply by excessive flow. When destructive fracture does occur, it follows the pattern of the carbide pistons.

Both types of pistons show appreciable dishing after runs approaching the maximum pressure. Figure 4 shows the profile of one pair of Kennametal K-6 cemented tungsten carbide pistons after several runs at 500°C, at a maximum pressure of 80 kb. These pistons have made many more runs at high pressure.

This dishing has no deleterious effect so far as we have been able to learn. On the contrary, it has two beneficial effects: (1) the central pressure is more uniform due to steeper pressure gradients at the periphery; (2) the sample thickness is greater—reaching .015″ in these pistons, independent of

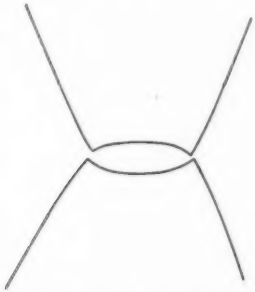


Fig. 4. Profile of Kennametal K-6 piston faces after several runs at 500°C-maximum pressure 80 kb (vertical exaggeration 5:1). Depression in center of piston face: .005". Where pistons are not of same size, area of smaller one is used in calculating pressure.

pressure. With dished pistons an excess of sample is always used, to be sure of filling the space between the pistons at pressure.

For temperatures up to 600°C, pistons made of ordinary high speed steel provide respectable pressures.

Above 1000°C, pressures attainable with this type of apparatus may be expected to decrease to about 10 kb at 1200°C with the best materials available. For higher pressures at the higher temperatures, localized heating of the sample will be necessary, so that the pistons will be cool in regions of high stress. In principle, any desired temperature may thus be reached at 100 kb. Bridgman's (1952) resistance apparatus indicates one method by which electrical heating might be used.

Pushers are made of Inconel X. Transite was initially chosen for thermal insulation of the push rods after tests of other similar materials. At high temperature and pressure, transite deforms and must be frequently replaced. It has recently been found that the thermal insulation provided by the transite is unnecessary, and these parts are now made of stainless steel.

It is desirable to design the apparatus so that it undergoes large elastic strain at pressure, in order to reduce the pressure rise due to thermal expansion on heating. This is done principally by making the press tie-rods long and of minimum cross section. The apparatus shown in plate 1 increases in pressure about 60 percent on heating to 600°C, due to the expansion of the pushers and piston holders which would amount to about 1/16 of an inch at constant pressure. Approximately one-third of the yield of the apparatus is extension of the tie-rods, one-third is compression of the pushers and piston assembly, and the remainder is due to bending of the end plates, compression of oil in the ram, etc.

It is necessary to water-cool the plate at the top of the ram to prevent heating of the oil in the ram, which would cause a rise in pressure. With this water turned off, a pressure rise at an initial rate of 50 percent per hour is observed after attaining a stabilized temperature. With the water on, pressure remains constant to a few percent.

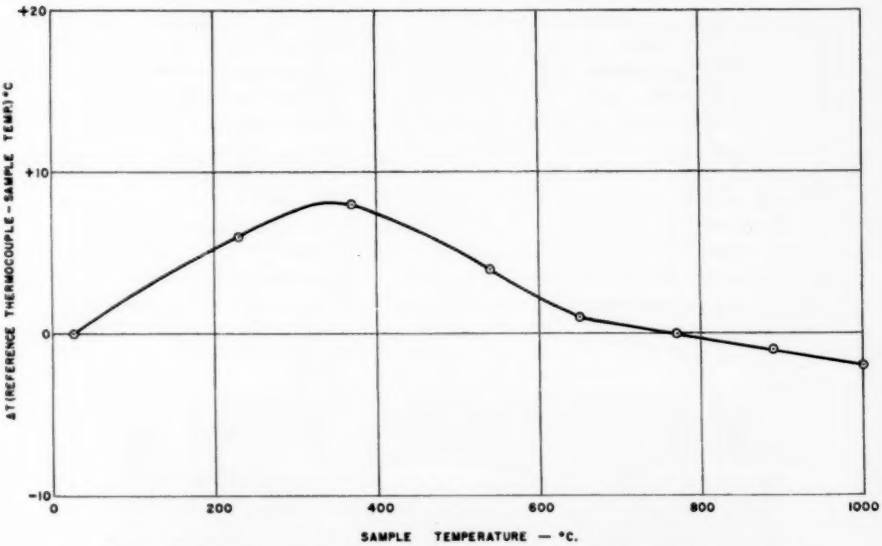


Fig. 5. Typical calibration curve showing difference between temperature of reference thermocouple and sample temperature as measured by thermocouple between piston faces under pressure.

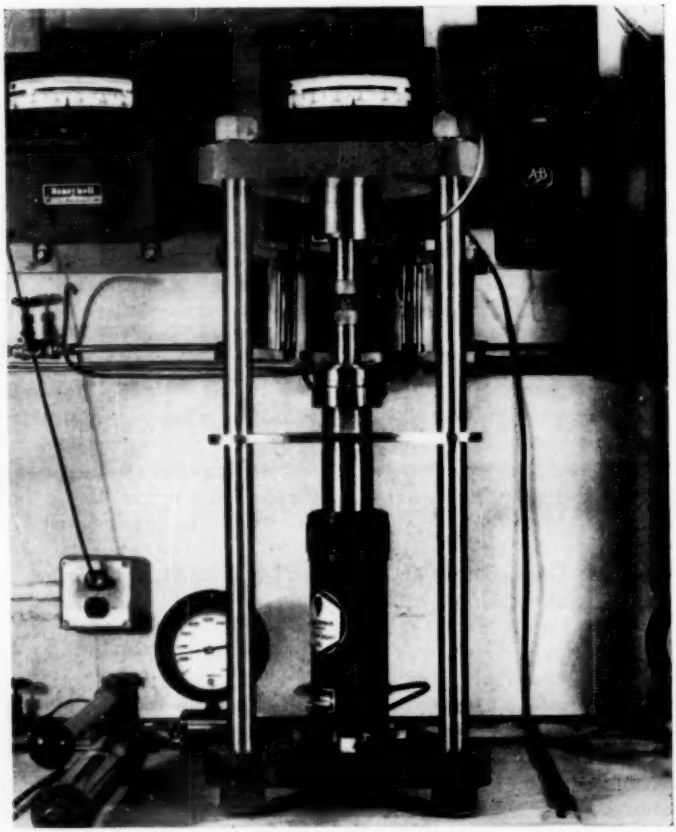
CALIBRATIONS

Due to the solid steel pushers there is substantial axial heat flow and consequently a moderately large temperature gradient away from the center of the furnace where the specimen is located. This could be mitigated by using a furnace wound much more heavily at the ends, or by the use of high-strength low-conductivity pusher material. These measures are expensive, however, and have been eliminated on finding that a reproducible sample temperature can be attained without them. The difference between sample temperature and reference thermocouple temperature is moderately sensitive to the position of the furnace. One-quarter of an inch difference in position of the furnace typically will change this difference by about 20°C. In practice, the furnace is positioned, by moving the hinges up or down, until the sample temperature as shown by a thermocouple between the pistons in the sample position is near the reference thermocouple temperature. A temperature calibration is then made, yielding a result like that in figure 5. This calibration is reproducible, so long as the apparatus is not changed. A new calibration is made after every change in the pistons, holders, or pushers. Thermocouple temperatures are recorded on a Foxboro six-point recorder which facilitates this calibration. It was found necessary to calibrate the recorder.

The force developed by the ram is determined by the bourdon gauge and the area of the ram. This is calibrated by inserting a Baldwin Southwark CXX precision load cell in place of the apparatus. It has been found that the U. S. Gauge Company gauges are initially within their stated tolerance of

0.5 percent of full scale, and that the friction on the Blackhawk rams is 1 percent. The Heise gauge is regularly used to check the U. S. gauges. It is desirable to measure the diameter of the piston faces to 1 percent or better, which we do with a cathetometer. One must be sure that there are no elements in the system which can introduce any undetermined friction or in any way bear any of the force which is thought to be applied to the specimen. In our apparatus, there are two such elements: the plate which aligns the ram (pl. 1), and the stainless steel ring. The alignment plate has been found by the above force calibration to introduce no measurable friction. The stainless steel ring clearly bears some load outside the piston face. This has been evaluated by measuring the deformation in the ring and roughly calculating the force required to produce this. The magnitude of this force varies with pressure, temperature, and sample size, but in our configuration it is always less than

PLATE 1



Apparatus, with furnace open to show piston assembly.

the force necessary to balance the pressure gradient at the periphery of the piston faces.

The corrections on central sample pressure with reference to the pressure calculated from force and initial piston area are approximately as follows:

Due to pressure gradient at periphery	+3%
Due to stainless steel ring	−2%
Due to elastic distortion of pistons	+1%

The net of these corrections appears to be within the uncertainty of pressure due to lack of precise knowledge of pressure distribution in the sample, so no correction is made. Near the limit of strength of the pistons, large plastic deformations can occur, resulting in increases of piston area by as much as 20 percent. The piston diameter must be measured after each run when in the region of flow. At very low pressures the correction due to the stainless ring can be much larger than 2 percent, and suitable precautions must be taken.

In assembling the pistons, sample, foil, and stainless ring, a split jig is used to insure alignment of all parts. This jig is removed only after several kilobars of pressure have been applied to the sample. From this point on there is no connecting member between the pistons save the sample and ring. There is thus no possibility that the force of the press can be borne by anything except the sample and ring.

SAMPLE PREPARATION

The sample is introduced in powder form. Platinum-10% rhodium foil .001″ thick is placed between the sample and the pistons, to prevent reaction with the pistons and to facilitate removal of the sample. At temperatures above 500°C, Molykote (MoS_2) is applied to the piston faces to prevent adhesion of the foil. A stainless steel ring is used around the periphery of the piston faces to retain the sample and volatiles and to provide a thicker specimen. The part of this ring between the piston faces is .010″ wide and .005″ thick. The geometry of a typical ring and sample assembly at low pressure is shown in figure 6. At high pressure, of course, the ring is squeezed down and partially extruded.

If the initial amount of the sample is not too great to fill the void, then the platinum-rhodium foils and the stainless ring are in direct contact, and the pressure deforms them, making a metal-to-metal seal. This was initially thought to be necessary to retain water vapor, but subsequent experience has shown that it is not usually needed.

At moderate to high pressures, the amount of sample present is not critical. An excess of sample can be added, provided it is not so much in excess that it results in a blow-out of the stainless steel rings. In practice, this means that the sample is ladled in with a spatula so that it forms a shallow rounded pile above the ring. The upper platinum foil is emplaced, the upper piston put in, and the assembly placed in the press. We are unable to discover any difference in results correlated with initial amount of sample, so long as the stainless ring remains in position. With excess sample, some is extruded past the stainless ring, forming an annular sheet perhaps .001″ thick. Diffusion of water

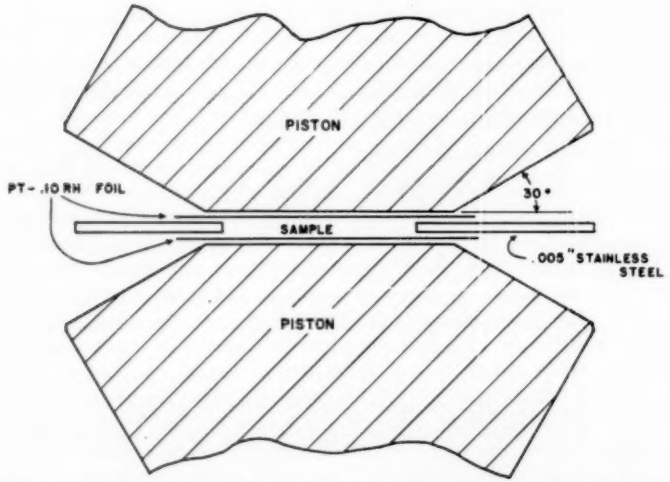


Fig. 6. Exploded assembly showing stainless ring, platinum foil, and sample geometry.

vapor through this extruded material is apparently so slow that it does not interfere with our experiments.

The sample comes out as a lenticular wafer .004"-.015" thick, weighing 1-10 milligrams. It is usually hard and coherent. Under the microscope its crystalline nature is usually evident. Grain size is usually 1-10 microns, so that some optical properties can be determined microscopically. Moderately good X-ray patterns can usually be obtained on a Norelco recording X-ray spectrometer. These X-ray determinations provide the easiest and most unequivocal means of identifying the crystalline phases present in the sample. It has been found that grinding the sample in a mortar before X-raying results in general in a better pattern. This is presumably due to the development of preferred orientation due to the shear stress and/or strain present in the sample under pressure.

PROCEDURE

Successful use of this apparatus requires appropriate quenching to preserve the sample in the crystal phase which it had attained at stabilized temperature and pressure. Quenching is normally done by swinging the furnace open and directing an air blast directly at the pistons. A cooling curve is shown in figure 7. Even this rapid rate of cooling is not sufficient to prevent recrystallization of some samples. Whenever the presence of water vapor or other volatiles is not necessary to preserve the crystal phase present during the run, the pistons and holders can be removed rapidly and water quenched. The sample in the stainless ring and platinum foil capsule usually separates readily from the piston, and quenching is essentially instantaneous on contact with water. The time to get the sample from test conditions into the water is less than 10 seconds.

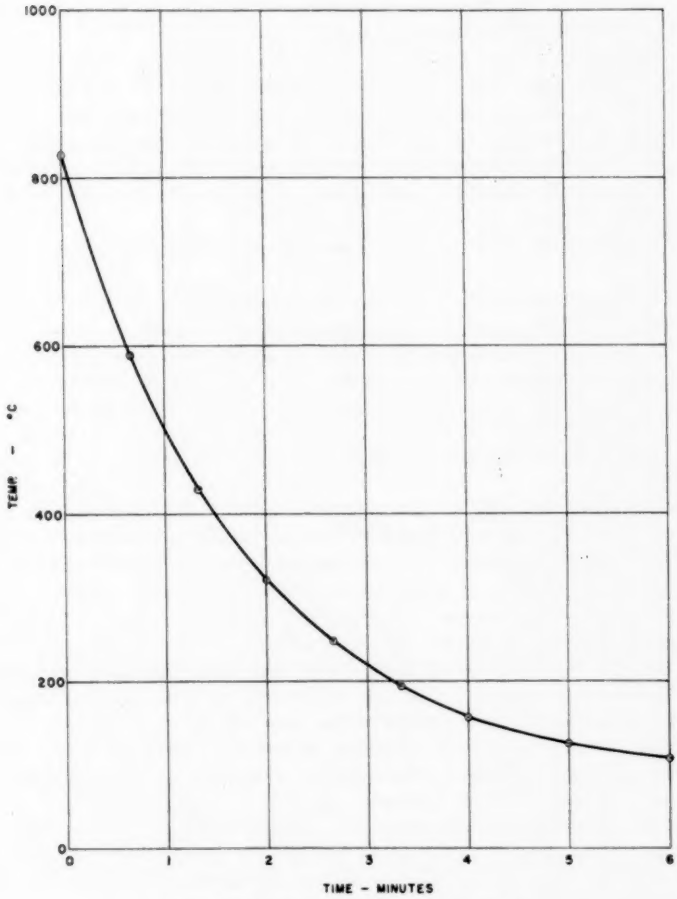


Fig. 7. Typical cooling curve with air jet.

Any phase boundary may be followed only over a limited range of temperature. At low temperatures the rate of reaction is too low to achieve equilibrium in times available. At high temperature, the reaction rate may be so great that quenching becomes impossible. Frequently the role of water may be exploited to extend this range. In exploring the analcite-jadeite + water equilibrium, it was found that at temperatures in excess of 500°C air quenching was too slow, and analcite recrystallized in the quenching process. In this instance, the problem was solved by releasing pressure before air quenching. Jadeite and nepheline albite were unchanged by release of water vapor, and analcite retained its skeleton structure as anhydrous analcite. The rate of re-

action drops very rapidly when water vapor pressure is released, so this expedient is frequently helpful in quenching.

We have found that equilibrium is not readily attained when the initial material is composed of more than one crystalline phase. We had hoped that the shear strain imposed on the aggregate during loading would provide sufficiently intimate mixing so that all components would come to equilibrium. This is not the case. It may well be that rotation of the pistons with respect to each other would promote the attainment of equilibrium due to the resultant intense shearing strain. We shall shortly try this.

We have found three satisfactory methods of introducing water into the system:

(1) Starting material is a hydrate of the composition intended for study (e.g. analcite for the reaction jadeite $\rightleftarrows$ nepheline + albite).

(2) Starting material contains a hydrate whose anhydrous product does not take part in the reaction to be studied (e.g. to study the reaction jadeite + water $\rightarrow$ analcite, start with diaspore + jadeite. The diaspore decomposes to corundum releasing water which combines with jadeite to form analcite. This will work only close to the diaspore-corundum boundary, in the corundum field.

(3) Starting material is glass with adsorbed water. Finely ground glass will absorb roughly 0.5 to 1 percent of water, which is bound to the glass even at elevated temperatures. This technique is not in general suitable for adding a known amount of water but is extremely useful in adding enough water to increase reaction rates. For example, glass of a basalt composition was run at 1000°C, 10 kb for one hour with no observable crystallization. This glass was wet but was not ground very fine. The same glass, with prior fine grinding under water, crystallizes completely in short times at temperatures as low as 800°C. It is presumed that this difference in reaction rate is due to the water adsorbed: the crystalline phases are anhydrous. Water vapor apparently also increases the reaction rate in certain solid-solid transitions.

Proof that equilibrium has been attained at a phase boundary is accomplished by standard techniques—e.g. demonstration that the reaction is reversible. In the case of dehydration boundaries, special techniques are required with this apparatus which are beyond the scope of this paper and will be reported in other papers dealing with such systems.

Experience to date indicates that at hydration-dehydration boundaries, the water vapor pressure closely approximates the total pressure. Such boundaries determined with this apparatus lie on a smooth extension of the boundaries determined at lower pressure in conventional hydrothermal apparatus.

We have the impression that reaction rates are faster in this apparatus than in a purely hydrostatic environment but do not yet have adequate information to prove this. MacDonald (in press), using our squeezer, found that the calcite $\rightarrow$ aragonite transition went to completion in about 15 minutes at 500°C, whereas in a hydrostatic test at the same pressure and temperature no conversion to aragonite was observed in two hours in an experiment by Griggs.

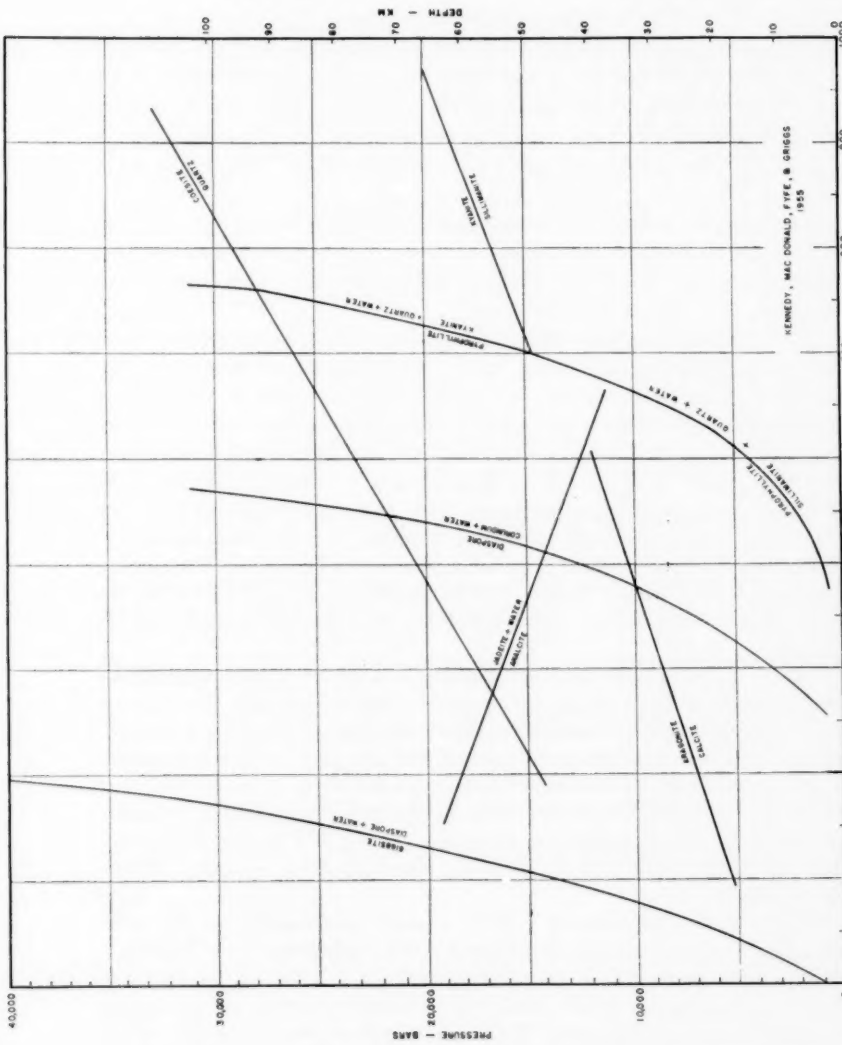


Fig. 8. Some phase boundaries determined with the squeezer. Each boundary is based on some fifty runs. Some of these results are tentative, subject to refinement, as work is still in progress. The dehydration curves are in all cases smooth extensions of boundaries determined below 2 kb in hydrothermal apparatus.

In our experiments to date, it has been found that any reaction which will go at all will usually go in one or two hours. We have, however, insufficient experience with long-term tests. If shear stress or strain is important in promoting reaction, one would expect that short-term tests would achieve nearly the same result as long-term tests in the squeezer, since there is a relaxation of shear stress with time. This effect will be tested explicitly in our new shearing apparatus.

UTILITY OF THE APPARATUS

Figure 3 shows the temperatures and pressures attained thus far. It is reasonable to expect that somewhat higher pressures may be attained in this apparatus in the future. Throughout the range of figure 3 satisfactory samples and equilibrium results have been attained except at low pressures. Below 5 kb, erratic results have been obtained with hydrous systems, indicating leakage of water.

Exclusive of auxiliary instrumentation, the apparatus itself is cheap—a few hundred dollars—or much less if a machine shop is available. It is extremely easy to use and requires little skill. Over 600 runs were made in our laboratory in the first year of operation.

The apparatus has been used to date mainly in determining equilibrium relations in solid-solid transitions and in hydration-dehydration reactions. Figure 8 shows some boundaries that have been explored at the time of this writing. The quartz-coesite and calcite-aragonite transitions were done by MacDonald (in press, 1956) in our laboratory. The former has been slightly modified in figure 8 as a result of further work by Kennedy from 600° to 900°C. The work on jadeite-analcite was done by Griggs, Fyfe, and Kennedy (1955). The work on gibbsite, diaspore, corundum, pyrophyllite, sillimanite, and kyanite was done by Kennedy. These studies will be described separately in publications to follow. Figure 8 is preliminary and may be revised by further work but indicates types of reactions which may be studied with the apparatus.

Based on Bridgman's findings, the accuracy of the pressure calculated from the observed force on the ram should be about 5 percent. No rigorous check has yet been made in our work. Two comparisons with other work have been made: MacDonald (in press) found that the pressure for the calcite-aragonite equilibrium as determined in our apparatus was about 1.5 kb lower than the value determined indirectly by Jamieson (1953). Kennedy's determination of the kyanite-sillimanite boundary (fig. 8) is almost identical with that found by Dr. Sydney Clark (personal communication) in Birch's hydrostatic apparatus.

Griggs, Fyfe, and Kennedy (1955) reported confirmation of the prior work of Robertson, Birch, and MacDonald (1955) on the jadeite = nepheline + albite equilibrium. Much subsequent work on this system by Kennedy indicates that our earlier results were in error owing to melting and that agreement can no longer be reported. Work on this is being continued and will be described later.

This apparatus is useful for rapid exploration of the stability fields of minerals at pressures and temperatures corresponding to those which are believed to exist in the outer 100-150 km of the Earth's crust and mantle in the normal Earth temperature gradient. The simplicity, ease of operation, and the short time required for each run should make it possible to expand greatly our knowledge of mineral stability at high pressure.

ACKNOWLEDGMENTS

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SURVIVAL OF PRIMITIVE NOTOUNGULATES AND CONDYLARTHS INTO THE MIOCENE OF COLOMBIA

MALCOLM C. McKENNA

ABSTRACT. The late Miocene La Venta fauna from Colombia has yielded fossil remains of a primitive isotemnid-like notoungulate and a didolodont condylarth, both forms representing late survival of essentially early Tertiary mammalian types. The condylarth, a new genus related to *Ernestokokenia* and *Asmithwoodwardia*, is the largest known form and represents the latest known occurrence of the order Hyopsodont affinites for *Ernestokokenia, Asmithwoodwardia,* and the new genus are discounted.

Stirton (1953) has published a preliminary report on the extensive late Miocene La Venta fauna from the upper Magdalena River valley southwest of Bogotá, Colombia. Most of the fauna has not been described, but papers by Cabrera (1929), Kraglievich (1928), Mook (1941), Reinhart (1951), Royo y Gomez (1942, 1946), Savage (1951a, 1951b), Stirton (1951), and Stirton and Savage (1950) have discussed some of the fauna in detail. In the present contribution a new genus of condylarth is described and a poorly represented primitive notoungulate is discussed. Both animals belong to groups known thus far only from the early Tertiary. Advanced interatheres, astrapotheres, toxodonts, and rodents indicate a post-Santacrucian age for the La Venta fauna; therefore it is believed that the occurrence of two primitive protungulates in the fauna indicates a long temporal range for these forms in the tropics, reminiscent of the occurrence of the hyaenodont creodont *Dissopsalis* in the late Tertiary Siwalik sequence in Pakistan. There is no strong evidence that either of the La Venta specimens has been reworked from older Tertiary deposits.

I wish to thank Mr. Richard Estes and Drs. D. E. Savage and R. A. Stirton for their criticism of the manuscript, and the staff of the Department of Geology and Paleontology at the American Museum of Natural History in New York for permitting me to study material from the Itaborai fauna in 1953. The illustrations are by Owen J. Poe.

Class MAMMALIA

Order NOTOUNGULATA

?Suborder TOXODONTA

?Family Isotemnidae, sensu lato

Undescribed genus and species

SPECIMEN: U. C. 42891, an eroded left M_3 with a portion of the hypoconulid chipped away. Found in a small concentration of remains which yielded about 100 teeth belonging to several kinds of rodents and assorted specimens representing crocodiles, fish, ?lizard, armadillo, ?glyptodont, small nothrothere, toxodontid, proterotheriid, and *Miocochilius*. Many of these fragments were water worn. All were dark brown in color.

LOCALITY: U. C. Loc. V-4525, in thirty-foot thick unit of alternating sandstones and claystones between the "Yellow Sandstone" and "Lower Red Bed" units south of Quebrada La Venta and traceable over the divide into the Rio Tatacoa drainage. Honda group, Department of Huila, Colombia.

FAUNA: La Venta.

AGE: Approximately Friasian, late Miocene.

DESCRIPTION: M_3 brachydont, incipiently lophodont; trigonid not extremely oblique, giving a nearly symmetrical outline instead of the typical advanced notoungulate oblique outline; trigonid occupying one-third or less of total length of tooth; paraconid absent; paralophid absent; metaconid high and marginal, placed more posteriorly than protoconid; metalophid without accessory cusp; hypoconid strong, placed more anteriorly than entoconid; entoconid marginal, with labially directed spur; hypoconulid elongate, with labial, anteriorly directed crest; anterior cingulum present, slightly cuspidate anterolingually; labial and lingual cingula very weak. Measurements: present total length of tooth 8.4 mm; estimated original total length 8.7 mm; height of metaconid above enamel base 5.5 mm; estimated height of hypoconid above enamel base 3.9 mm; maximum width of trigonid 5.2 mm; maximum width of talonid 4.4 mm.

COMMENTS: This specimen is apparently a primitive notoungulate allied to the primitive Isotemnidae (including the Oldfieldthomasiidae as a subfamily) and to such forms as *Henricosbornia*. Of the characters listed above, the shape of the trigonid, the lack of a metalophid accessory cusp and paraconid, and the presence of a labially directed entoconid spur seem most diagnostic, and point to relationship with primitive notoungulates like *Colbertia* de Paula Couto 1952a rather than to didolodonts or to lithopterns like *Wainka* or the referred specimens of *Protheosodon* figured by Loomis (1914, p. 42). Comparison with *Colbertia* is more favorable than with any other notoungulate genus, chiefly because in *Colbertia* the trigonid is less oblique than in such forms as *Henricosbornia*, *Notostylops*, and *Othnielmarshia*.

Stirton (1953, p. 614) considered the specimen a member of the La Venta fauna but suggested that it could possibly have been redeposited from older fossil-bearing rocks. This consideration was based on the primitive nature of the tooth, not on the fact that it appears to be peculiarly worn (Stirton, personal communication). Those surfaces in which wear occurs (other than that caused by occlusal attrition) show a smooth, even removal of enamel suggestive of solution rather than abrasion. Other than this wear, the tooth is quite well preserved, with no cracks in the enamel of the crown. In other details the specimen is preserved in precisely the same manner as other teeth from the same locality.

Order CONDYLARTHRA

Family Didolodontidae

Megadolodus molariformis, new genus and species

ETYMOLOGY: *Mega* Gr. large, great: *dolos* Gr. deceit; *odontos* Gr. tooth; *molariformis* L. shaped like a molar. In allusion to the large size of the genus, its relationship to the Casamayoran genus *Didolodus*, and to the uniquely advanced fourth lower premolar.

TYPE OF GENOTYPIC SPECIES: U. C. 39270, a fragmentary left mandible bearing M_1, the labial side of P_4, and the roots of P_3, M_2, and M_3.

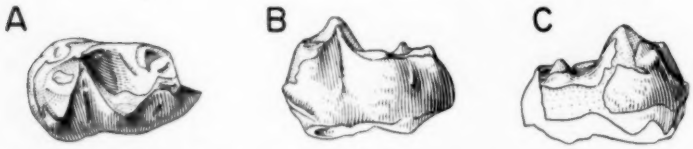

Fig. 1. Undescribed genus and species of ? Isotemnid, U. C. 42891, U. C. Loc. V-4932, La Venta fauna, Colombia. Left M_3. A., occlusal; B., labial; and C., lingual views. × 3.

TYPE LOCALITY: U. C. Loc. V-4932, 200 yards northeast of the railway bridge at kilometer 126 across Quebrada Balsillas, Neiva-Girardot Railway, 11 kilometers northeast of Villavieja, Department of Huila, Colombia. Variegated gray, buff, and rusty claystone containing much calcareous material, including nodules and concretions. San Nicolás unit, Honda group.

FAUNA: La Venta.

AGE: Approximately Friasian, late Miocene.

GENERIC AND SPECIFIC DIAGNOSIS: Easily the largest known condylarth; depth of jaw twice that of *Phenacodus primaevus* and *Paulogervaisia mamma* and three times that of *Didolodus multicuspis*. M_3 estimated 20 percent larger than that of *Paulogervaisia inusta*, the largest previously known condylarth. Measurements: P_3 estimated talonid width 9 mm; P_4 length 15.6 mm, estimated width 14 mm; M_1 length 16.5 mm, trigonid width 16.1 mm, talonid width 15.8 mm; M_2 estimated length 19 mm, estimated trigonid width 17 mm, estimated talonid width 16 mm; M_3 estimated trigonid width 18 mm. Jaw robust, depth under M_1 47 mm, maximum thickness below M_3 23 mm. ?Two mental foramina: one definitely below the talonid of P_4, possibly a second anterior to this, below the trigonid of P_4.

P_4 fully molariform, in contrast to all other members of the Didolodontidae and Phenacodontidae; trigonid robust, but not as large relative to the talonid as in *Didolodus*, *Ernestokokenia*, or *Asmithwoodwardia;* paraconid probably missing; protoconid a large, blunt cone giving rise to a paralophid typical of *Ernestokokenia*, *Asmithwoodwardia*, *Hyopsodus*, many phenacodonts, and some periptychids and arctocyonids; anterior cingulum weak; talonid with strong hypoconid and anterolingually directed metalophid bearing a trace of an accessory cusp; labial cingulum weak, non-cuspidate; hypoconulid probably weak; labial enamel moderately vertically crenulated.

M_1 with robust but short trigonid; paraconid totally absent; protoconid smaller than metaconid, connected to the latter by a strong, looping paralophid, as in P_4; anterior cingulum strong; talonid with strong hypoconid and anterolingually directed metalophid apparently lacking an accessory cusp, but with a small cuspule developed labial to it between the hypoconid and protoconid; entoconid opposite to and weaker than hypoconid, possessing strong anterior ridge directed toward metaconid; hypoconulid strong, with strong cingula directed downward both labially and lingually; labial cingulum developed only around base of protoconid and most anterior portion of base of hypoconid; lingual cingulum absent; labial enamel

moderately vertically crenulated, lingual enamel heavily crenulated in upper portions, especially on the metaconid, where three folds in the enamel are present. M_2 larger than M_1. M_3 as large as, or larger than M_2.

COMMENTS: The Miocene genus *Megadolodus* possesses a dentition which could belong only to a primate, primitive artiodactyl, arctocyonid, or condylarth. From the first three of these groups *Megadolodus* is differentiated by its possession of both a wide talonid basin and a distinctive looping paralophid connecting the protoconid to the metaconid. Both of these characters are possessed by certain Paleocene and Eocene arctocyonids and condylarths. Among these latter forms *Ernestokokenia*, *Asmithwoodwardia*, and some of their less well known relatives are closely similar to *Megadolodus* in known morphology. It is to these early Tertiary forms that we must turn for close comparison.[1]

The well known Casamayoran genus *Didolodus* differs from *Megadolodus* in that P_4 shows no indication of becoming molariform, a paraconid is present on the molars, a strong, litoptern-like metalophid accessory cusp is developed, the molars are somewhat more elongate, and the size of the animal was smaller.

The Riochican and Casamayoran genus *Ernestokokenia* (?including *Archaeohyracotherium*) is now fairly well known, thanks to the work of de Paula Couto (1952b). *E. parayirunhor* de Paula Couto differs from *Megadolodus* in that P_4 is somewhat less molariform (although much more molariform than in *Didolodus* or *Paulogervaisia*), a trace of a paraconid remains on the molars, the teeth are relatively narrower, the mental foramina are differently situated, and the size is considerably smaller.

Asmithwoodwardia, once one of the most poorly known didolodonts, is now the best known (de Paula Couto, 1952b). It occurs in the Riochican Itaborai fauna and in the Casamayor fauna. It is the smallest didolodont, whereas *Megadolodus* is the largest, but the two genera are comparable in important details. The P_4 of *Asmithwoodwardia* is considerably less molariform than in *Megadolodus* and somewhat less molariform than in *Ernestokokenia*. It is more molariform than in *Didolodus*. M_1 of *Asmithwoodwardia* lacks any trace of a paraconid, as in *Megadolodus* and the North American Eocene genus *Hyopsodus*. No metalophid accessory cusp is present, in agreement with the condition in *Megadolodus* and the Itaborai species of *Ernestokokenia* and in contrast to the condition in *Didolodus*, *Lamegoia*, some phenacodonts, and many of the more advanced species of *Hyopsodus*. As in *Ernestokokenia*, the molars of *Asmithwoodwardia* are more elongate than the quadrate molars of *Megadolodus*. Finally, the looping paralophid in *Asmithwoodwardia* is closely similar to that of *Megadolodus* and *Ernestokokenia*, as well as to that of *Hyopsodus* and some of the phenacodonts.

Megadolodus is morphologically more similar to *Ernestokokenia* and *Asmithwoodwardia* than to such forms as *Didolodus*, *Lamegoia*, and *Paulogervaisia*. This similarity is accepted here as indicating actual relationship.

[1] Stirton (1947) has described a new genus, *Lophiodolodus*, from the Oligocene Chaparral fauna, found near Tolima, Colombia, comparing it with the didolodonts. I suspect that *Lophiodolodus* is a sirenian; for this reason the genus does not enter into the present discussion.

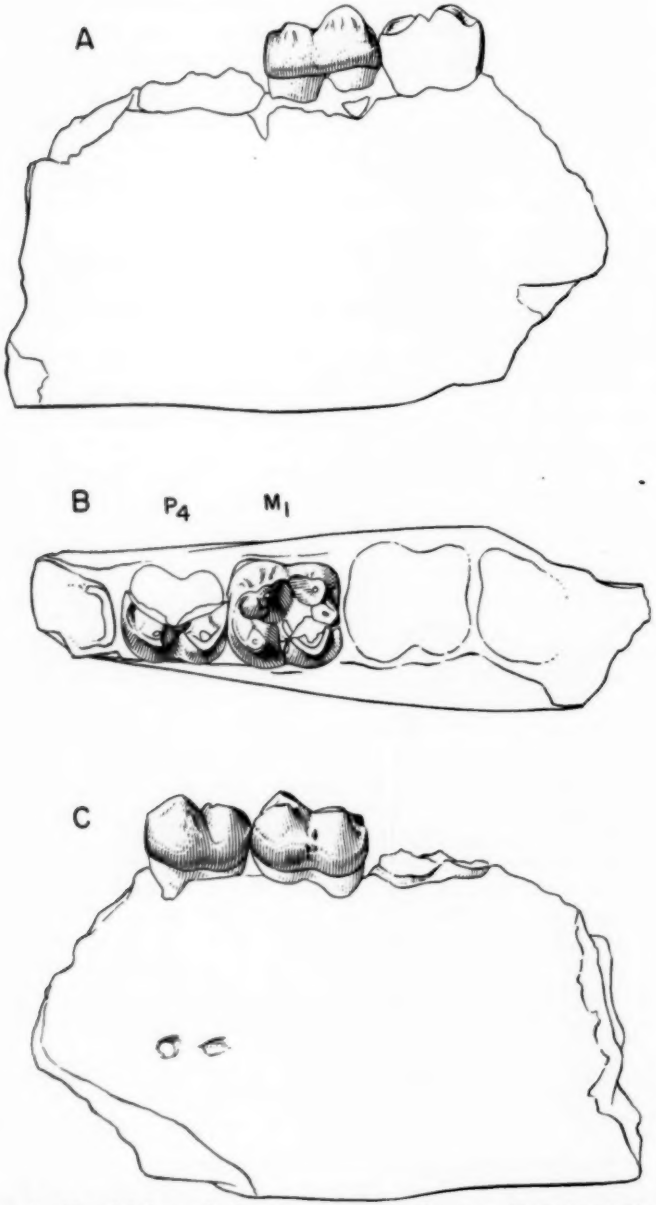

Fig. 2. *Megadolodus molariformis*, new genus and species, U. C. 39270, U. C. Loc. V-4932, La Venta fauna, Colombia. Left lower jaw fragment bearing P_4 and M_1. A., lingual; B., occlusal; and C., labial views. × 1.

At least two lineages may be discerned within the group of genera now formalized as the family Didolodontidae. In the lineage exemplified by *Didolodus, Lamegoia, Paulogervaisia, Proectocion*, and their less well known allies and synonyms a rather litoptern- and notoungulate-like specialization was attained in some structures, but in so far as is known, there was no tendency toward molarization in P_4. In the lineage exemplified by *Megadolodus, Ernestokokenia*, and *Asmithwoodwardia* an essentially arctocyonid-like morphology was retained, but a tendency toward molarization in the fourth premolars developed. The molar paraconids became lost and a *Hyopsodus*-like paralophid developed.

This interpretation is in opposition to that of de Paula Couto (1952b), who proposed the novel and exciting view that *Asmithwoodwardia* is actually a hyopsodont and not a didolodont at all. His viewpoint is not to be passed over lightly. It has such important implications for protungulate classification and zoogeography that his principal conclusions are summarized below.

1. "*Asmithwoodwardia* is so similar to the North American Paleocene-Eocene Hyopsodontinae, in its general characters, and especially in the dental structure, that, in my opinion, the classification of this genus in this group is in complete accordance with its real affinities."

2. "The size of *A. scotti* is close to that of *Hyopsodus lepidus*, from the Bridger beds. . . . "

3. "If [the remains of *A. scotti*] were accidentally found in North America, they would probably be considered as representing a new species of this small North American . . . Eocene relative."

4. " . . . The differences between *Asmithwoodwardia* and the Paleocene-Eocene North American forms classified in the subfamily Hyopsodontinae are merely of generic rank. . . . "

5. *Ernestokokenia* is more closely allied with the most primitive Phenacodontidae than with the Hyopsodontidae. *Asmithwoodwardia* is a hyopsodont. Ergo, the two genera are not related.

6. *Ernestokokenia* is much larger than *Asmithwoodwardia* but agrees well in size with the most primitive Phenacodontidae.

7. *Ernestokokenia* resembles the phenacodonts in the structure of $P\frac{3\text{-}4}{3\text{-}4}$ more closely than does *Didolodus* but is retained in the Didolodontidae.

De Paula Couto's first point is over-generalized. The only members of the Hyopsodontinae that *Asmithwoodwardia* resembles are *Haplaletes* and the type genus *Hyopsodus* itself. This resemblance is not closer than that of *Asmithwoodwardia* to *Ernestokokenia*. In particular, the arctocyonid-like aspect of the molars, the projecting hypoconulid of M_3, the size of the canine, the shape of the incisor crowns, the heel of P_4, and the structure of P^3 in *Asmithwoodwardia* are not at all suggestive of hyopsodont relationships.

With regard to the second point, it might be pointed out that at least one species of *Hyopsodus, H. powellianus*, is actually larger than *Ernestoko-*

kenia parayirunhor, let alone *Asmithwoodwardia*. Size is an important character, but it should not be over-emphasized.

The accuracy of point 3 is a matter of opinion and should be decided for himself by each worker. Personally, I would give *Asmithwoodwardia* generic rank if it were found in North America, and would give serious consideration to the thought that it might be an arctocyonid rather than a hyopsodont. This argument applies to point 4 as well.

While de Paulo Couto does not explicitly state point 5, its conclusion is implied. The conclusion is a non sequitur based on the a priori premise that *Asmithwoodwardia* actually is a hyopsodont.

With regard to de Paula Couto's sixth point, while it is admitted that *Ernestokokenia* compares favorably in size with such primitive phenacodonts as *Tetraclaenodon minor* and other small forms, the size difference between *Asmithwoodwardia* and *Ernestokokenia parayirunhor* is only about 40 percent. De Paula Couto himself has created two new species of *Ernestokokenia* which differ in size by more than this.

In addition to de Paula Couto's statement in point 7, it should be pointed out that there is a strong arctocyonid resemblance in the morphology of *Ernestokokenia*, e.g., compare with *Thryptacodon* and its allies.

Discovery of the gigantic new Miocene genus *Megadolodus* sheds important new light on the question of the interrelationships of *Ernestokokenia* and *Asmithwoodwardia*. Now a third South American genus is known in which the anterior portion of the molar trigonids has assumed an *Hyopsodus*-like aspect. All three South American forms are believed to be closely related. Either all three are advanced hyopsodonts and a drastic re-evaluation of that group is necessary or all three are didolodonts of an essentially primitive sort that have converged to a degree with a particular genus of a distant North American family.

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ARGON-POTASSIUM DETERMINATION OF THE AGE OF THE BOULDER BATHYLITH, MONTANA

ADOLPH KNOPF

ABSTRACT. An argon-potassium determination of the age of the Boulder bathylith of Montana shows that the prevailing granodiorite of the bathylith is certainly more than 65 million years old, and most probably 87 m y. This determination is of the same order of magnitude as zircon alpha-count determinations on the granodiorite, and is compatible with the geologic evidence (post-Niobrara or post-Montana, pre-Oligocene).

Dr. J. H. Reynolds, of the University of California at Berkeley, and Dr. R. E. Folinsbee, of the University of Alberta, have kindly determined by the argon-potassium method the age of the granodiorite that makes up the larger part of the Boulder bathylith. The bathylith, as elsewhere pointed out (Knopf, 1953), is a composite mass, made up of successive intrusions. The first member is a basic hypersthene granodiorite of 61.14 percent silica content and density 2.78. This basic granodiorite was invaded by a younger, more silicic granodiorite of 65.49 percent of silica content and density 2.71. A specimen of the younger granodiorite was obtained at the Kain quarry on Clancy Creek, one mile west of Clancy and 14 miles southeast of Helena. This granodiorite forms the prevailing kind of rock that makes up the bathylith, as at Butte, Elkhorn, Elk Park, and Clancy. It has been chemically analyzed at the Rock Analysis Laboratory of the University of Minnesota in 1951.

A specimen of this granodiorite containing a small pegmatitic schlier rich in potassium feldspar was sent to Dr. Folinsbee, who was then at the University of California engaged on a research project of absolute age determinations by the argon-potassium method. Dr. Folinsbee prepared a sample for analysis as follows: The feldspar veinlet was sliced off, crushed, and magnetically separated to give an orthoclase-quartz concentrate. The potassium content of the concentrate was determined to be 8.21 percent, the average of two closely agreeing photometer determinations. The argon content was determined by means of a mass spectrometer by Dr. Reynolds, who reports as follows (letter dated November 2, 1955):

"Sample number: KA-34 — Date of argon extraction 10/26/55
Sample mesh: 20-100 — Sample weight: 6.03 grams
Magnetic separator: 1.7 amperes — A^{40} (radiogenic)/K^{40}: .00399±.00012
Per cent Potassium: 8.21±.08 — Per cent atmospheric argon in final gas sample: 21.0

"To compute the most probable age of this sample, we use a branching ratio of 0.089, determined empirically by the argon content of pegmatitic feldspars of known age. Such a calculation yields 87.2 million years.

"The true branching ratio of K^{40} is 0.11 ± .01. The age computed using this constant is correct only if there has been no argon leakage in this sample, and thus represents a *lower limit* to the age. This age is 70.8 ± 6.5 million years.

"In other words, this sample has a most probable age of 87 million years and is almost certainly older than 65 million years."

Recently five age determinations based on alpha-counting and measurement of the lead content of zircon and monazite obtained from rocks of

the Boulder bathylith have been reported by Chapman, Gottfried, and Waring (1955). They range from 61 to 72 million years. The lowest as well as the highest "ages" were obtained for presumably the youngest member of the intrusive sequence in the bathylith, namely, an alaskite near Elkhorn Peak, for which the age determined on zircon is 61 m y and that based on monazite from the same alaskite is 72 m y. However, the reliability of an age determination in years based on zircon by alpha-counting appears to be remarkably uncertain. Tilton and Aldrich (1955) have recently discussed the reliability of zircons as age indicators, basing their argument on six zircon samples for which the isotopic composition of the radiogenic leads was determined. The four "ages" that therefore can be calculated for each sample proved in general to be astoundingly discrepant.

The geologic age of the Boulder bathylith is known to be post-Niobrara, based on marine fossils obtained by me in 1947, and identified as of "Upper Colorado (Niobrara) age" by Dr. J. B. Reeside (letter dated March 29, 1948), and is further known to be probably post-Montana, based on leaves found by J. B. Lyons (1944) in the Adel Mountain volcanics, which are the youngest rocks cut by the bathylith. By earliest Oligocene time the bathylith had been uncovered by erosion, for at Pipestone Springs the well known vertebrate-bearing beds (Wood and others, 1941, p. 11, 28) containing an early Chadronian fauna (earliest Oligocene) rest on the granodiorite. The potassium-argon age here reported suggests that the Boulder bathylith was emplaced in very late Cretaceous time. Closer placement in the absolute geologic time scale will depend on the determination of what stratigraphically represents the end of Cretaceous time and the definitive determination of the absolute age of that horizon, be it topmost Maestrichtian or topmost Danian.

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ARAGONITE SPELEOTHEMS AS INDICATORS OF PALEOTEMPERATURE*

GEORGE W. MOORE

ABSTRACT. Many limestone caves in western United States contain aragonite speleothems (cave formations) which are now being covered by calcite deposits. These caves containing unstable aragonite lie in an irregular belt that extends east from the Pacific Coast. South of this belt aragonite speleothems are forming today, and north of it caves have no aragonite. Because, within the range of normal temperature, aragonite is thought to be the high-temperature form, and calcite the low-temperature form of calcium carbonate, the evidence suggests that western United States was warmer in the past than at present. Estimates based on the rate of growth of calcite speleothems coating aragonite deposits place the time of the warm period at the Thermal Maximum (Climatic Optimum), about 5000 years ago. Comparison of the present temperature of caves containing unstable aragonite with that of caves in which aragonite is forming today suggests that the average annual temperature of western United States at the time of the Thermal Maximum was about 15°F warmer than the present average annual temperature.

Some factors other than temperature that might affect the deposition of aragonite and calcite are also considered, and a brief survey is made of the crystal chemistry of calcium carbonate.

INTRODUCTION

A deep limestone cave has a temperature that is not affected by daily or seasonal variations in the temperature of the surface. The temperature of a cave represents approximately the average annual temperature of the region in which the cave lies and is determined chiefly by latitude and altitude (Davies, 1953, p. 9). By analogy, caves also may have reflected ancient average temperature in the geologic past. If this is true, cave deposits might be used to indicate the climatic history of a region.

Studies of the sequence of alternating travertine and clay layers in certain caves have given significant information on the record of wet and dry periods but have revealed little about past temperature. Fossil mammals found in caves have also been used to suggest contemporary environmental conditions, but the ability of these animals to adapt themselves to changing climates decreases the usefulness of this method. The present investigation is concerned with the possible use of the polymorphism of calcium carbonate to indicate ancient temperature conditions.

Calcium carbonate ($CaCO_3$) is almost always present in secondary deposits in limestone caves. It occurs as calcite and aragonite—two minerals that have the same chemical composition but different crystal forms. Temperature may be a factor in determining whether calcium carbonate is deposited as calcite or aragonite. A study of the mineralogical composition of stalactites, stalagmites, and other speleothems[1] in a group of widely spaced caves in western United States has revealed that the presence or absence of calcite and aragonite in these cave deposits shows an areal pattern. From this pattern the paleotemperature of the region has been inferred.

* Publication authorized by the Director, U. S. Geological Survey.

[1] A general term synonymous with the popular expression "cave formations." It is applied to secondary mineral deposits in caves (Moore, 1952).

Many suggestions on various parts of this problem were received from R. F. Flint and Horace Winchell of Yale University and from H. S. Yoder, Jr. of the Geophysical Laboratory, Carnegie Institution of Washington. Their generous help is gratefully acknowledged. I should also like to thank A. L. Lange of the Western Speleological Institute and E. A. Danehy, W. R. Halliday, and others of the National Speleological Society for assistance in the field work.

DISTRIBUTION OF SPELEOTHEMS IN WESTERN UNITED STATES

Some caves in the Pacific Coast, Great Basin, and Rocky Mountain Regions of western United States were examined to ascertain the mineralogy of secondary calcium carbonate deposits. Only large caves were chosen in which a reasonable degree of temperature stability could be expected. The area of the investigation has extremes of climate and altitude and therefore probably is as suitable an area for this type of investigation as any in the world. Mineral identifications were made by field determination of crystal morphology. Most of the determinations were later checked in the laboratory by measurements of refractive index.

A striking result of these examinations is that many caves preserve aragonite where only calcite deposits are forming today. Helictites and stalactites of aragonite, evidently formed under different conditions in the past, are being partly coated and in some cases nearly obliterated by present-day deposition of dripstone of calcite. The caves that contain unstable aragonite[2] occur in an irregular belt that extends from the Pacific Coast eastward through the central part of western United States. Reconnaissance shows that caves containing unstable aragonite speleothems also lie in a continuation of this belt to the Atlantic Coast at about the same latitude, and a review of the literature suggests that caves in similar temperate parts of the world also contain unstable aragonite. This report is concerned only with western United States.

North of the belt of caves containing unstable aragonite there are large limestone caves with speleothems of calcium carbonate. Examination of some of these caves revealed that all the deposits are composed of calcite and that none of the caves contain aragonite. On the other hand, in the area south of the unstable aragonite belt there are caves in which aragonite is forming today.

Because calcium carbonate speleothems in the north are calcite, in the south are aragonite, and in an intermediate belt are calcite and aragonite, it seems that cave temperature may play a part in determining which of these two minerals is deposited. It has been known for many years that within the range of normal temperature aragonite is more likely to form at high temperature than calcite (Rose, 1837). In a series of laboratory experiments, Murray (1954) recently confirmed the idea that high temperature favors aragonite and established the effect of some other variables on the precipitation of calcite and aragonite.

[2] For the purposes of this report, *unstable* aragonite is aragonite formed in the past where calcite is now forming. *Metastable* aragonite is aragonite now being deposited.

TABLE 1
Character of Aragonite in Caves

Cave and state	No aragonite	Unstable aragonite	Metastable aragonite
Washington			
1. Mt. Olive Cave	X		
California			
2. Samwel Cave	X		
3. Stone Man Cave	X		
4. Cave City Cave	X		
5. Mercer Caverns		X	
6. Soldiers Cave	X		
7. White Chief Cave	X		
8. Titus Canyon Cave			X
Nevada			
9. Northumberland Cave		X	
Utah			
10. Logan Cave		X	
11. Timpanogas Cave		X	
12. Oak City Cave		X	
Arizona			
13. Allen Springs Cave		X	
Montana			
14. Lewis and Clark Cavern	X		
Wyoming			
15. Frost Cave	X		
16. Table Mountain Cave	X		
Colorado			
17. Cathedral Cave	X		
18. Fairy Cave	X		
19. Hubbards Cave	X		
20. Wilson Cave	X		
21. Cave Creek Cave		X	
22. Cave of the Winds		X	
23. Porcupine Cave	X		
New Mexico			
Carlsbad Caverns			
24. Lunch Room		X	
25. Left Hand Tunnel			X
South Dakota			
26. Crystal Cave	X		
27. Stage Barn Caverns	X		
28. Rushmore Cave	X		
29. Wind Cave		X	

The character of speleothems in the caves examined in this study is given in table 1. The relation between isotherms of the present average annual surface temperature and caves that contain no aragonite, unstable aragonite, and metastable aragonite is shown in figure 1.

The present 45°F isotherm was found to separate all caves containing unstable aragonite to the south from those containing no aragonite to the north. A fairly large number of caves are near this line, establishing good control. The 60°F isotherm separates caves containing unstable aragonite from those to the south in which aragonite is forming today. This line is less

well established as it is based on only two caves. Titus Canyon Cave near Death Valley, California, in which aragonite is forming, has a temperature of 70°F. This is the warmest cave studied. Carlsbad Caverns, New Mexico, have a temperature of 56°F throughout most of their extent, and in these parts of the Caverns, calcite speleothems are forming on unstable aragonite. In the Left Hand Tunnel of Carlsbad Caverns, however, Black (1953) reported floating rafts of aragonite on a cave pool which has a temperature of 63°F (R. T. Hoskins, written communication, 1953). These deposits are destroyed by the slightest movement of the water so their presence in this frequently visited passage suggests that they are forming today. The transition temperature between calcite and aragonite in the environment of Carlsbad Caverns therefore seems to lie between 56 and 63°F. In figure 1 the average value of 60°F is used.

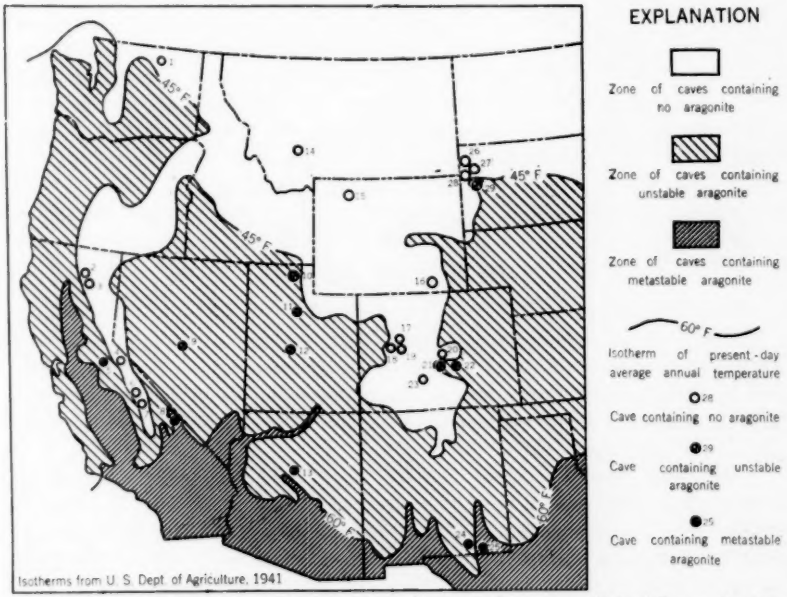

Fig. 1. Distribution and character of speleothems in western United States showing relation to surface temperature.

DISTRIBUTION OF SPELEOTHEMS AND PALEOTEMPERATURE

As aragonite is favored by high temperature and is preserved in caves that are now too cold for the formation of aragonite, the climate must have been warmer at some time in the geologic past. The present position of the 45°F isotherm evidently was occupied at some time in the past by the isotherm marking the northern limit of aragonite formation today: the 60°F isotherm. It seems from this evidence that the temperature in western United

States was about 15°F warmer at the time of deposition of the aragonite speleothems than it is today.

The rate of growth of the calcite speleothems covering the now unstable aragonite can be used to determine the age of this warm period. Coleman (1945) and Hicks (1950) have shown that stalactites grow in length at an average rate of approximately 0.1 inch per year. At this rate all the late calcite deposits were very likely formed since the last glacial maximum and perhaps even within the last few thousand years. The only important warm period since the last glacial maximum was the Thermal Maximum (Climatic Optimum) of about 5000 years ago (Flint, 1953). Accurate dating must await Carbon 14 determinations, but it is tentatively suggested that the aragonite deposits were formed during the Thermal Maximum and that the later calcite deposits were formed during the more recent cooler period.

Estimates made by other methods of the temperature that prevailed during the Thermal Maximum give values lower than that found in this investigation. Analyses of pollen in peat bogs in Scandinavia have indicated that average summer temperatures were 2.5°F higher than those at present (Flint, 1947, p. 491). Deposits of marine mollusks in a fiord in Norway indicate a maximum of 4.5°F above the present average temperature (Brögger, 1900-1901). It is possible that the value of 15°F obtained from the analysis of speleothems results from the fact that the region studied is a continental one subject to greater temperature fluctuations than the marine climate of Scandinavia. But recent studies of soils by Richmond (1953) give a value of only 5.8°F for the Thermal Maximum of an area in Utah.

ROLE OF TEMPERATURE IN THE POLYMORPHISM OF CALCIUM CARBONATE

The evidence obtained from cave deposits has supported the opinion that aragonite in nature is favored by relatively high temperature. Some facts that will be given later, however, lead to the opposite conclusion that *calcite* is the high temperature form of calcium carbonate. A resolution of this apparent paradox is attempted below.

The geochemical relations between calcite and aragonite, though they have perhaps been studied more than those of any other polymorphous series, still are not fully understood. Although aragonite seems to be the high-temperature mineral as inferred from laboratory experiments and from its natural occurrence in hot spring deposits (Allen and Day, 1935, p. 357) and tropical marine deposits (Sverdrup, Johnson, and Fleming, 1942, p. 998), calcite seems to be the high-temperature mineral on the basis of theoretical considerations (Jamieson, 1953; Thompson, 1955, p. 69).

Calcium has a coordination number of 6 in calcite and 9 in aragonite (Wyckoff, 1948). Hence calcite, which has lower coordination, should be favored by high temperature and low pressure (Buerger, 1948, p. 115). Again, the lower density of calcite suggests it is the high-temperature form. And finally, equilibrium studies give further support to the conclusion that calcite, not aragonite, is the high-temperature mineral (Jamieson, 1953; MacDonald, 1955). The stability range for aragonite at atmospheric pressure,

according to Jamieson, lies only below –197°C! All aragonite in nature, as a consequence, must have formed metastably.

The control of the polymorphism of calcium carbonate by temperature may result from the influence of temperature on the ratio between the ionic radii of calcium ion and carbonate ion. Calcite is rhombohedral and aragonite is orthorhombic. The rhombohedral structure is suited to cations of small ionic radius, and the orthorhombic to cations of large ionic radius (Evans, 1948). Table 2 is a list of the carbonate minerals giving the crystal form of each and the ionic radii of the cations. All the elements with ionic radii less than 0.99 angstroms form rhombohedral carbonates, and those with ionic radii greater than 0.99 angstroms form orthorhombic carbonates. Calcium carbonate is the only natural compound having both structures, and calcium has an intermediate ionic radius of 0.99 angstroms. At very low temperatures calcium carbonate may crystallize with the aragonite structure, but with increasing temperature the thermal vibrations of the ions increase, resulting in an increase in the effective ionic radii of calcium ion and carbonate ion. If the carbonate ion increases in size faster than the calcium ion, calcite is formed.

TABLE 2

Relation of Ionic Radii of Cations to Crystal Structure of Carbonates

Carbonate	Ionic radius of cation (angstroms)	Rhombohedral crystal structure	Orthorhombic crystal structure
$MgCO_3$	0.65	Magnesite	
$CoCO_3$	0.72	Cobaltocalcite	
$ZnCO_3$	0.74	Smithsonite	
$FeCO_3$	0.75	Siderite	
$MnCO_3$	0.80	Rhodochrosite	
$CdCO_3$	0.97	Otavite	
$CaCO_3$	0.99	Calcite	Aragonite
$SrCO_3$	1.13		Strontianite
$PbCO_3$	1.21		Cerussite
$BaCO_3$	1.35		Witherite

It is known from laboratory experiments, however, that, within the range of normal temperature, *aragonite* is favored by high temperature (Rose, 1837; Murray, 1954).

The formation of aragonite outside its stability range results from the presence of impurities (Zeller and Wray, 1956). Traces of barium, strontium, or lead, in solution, are essential for the formation of aragonite at normal temperature, possibly by crystal wedging. The likelihood that wedging is a factor in the formation of aragonite is supported by the observation that aragonite transforms to calcite at 450°C (Gruver, 1950). This transformation results from the release of impurities at elevated temperature.

As barium, strontium, or lead is needed for aragonite formation, presumably they are available in limestone cave solutions. Evidently moderately high temperature favors the incorporation of these ions and the formation of

aragonite. More work is needed to determine the threshold quantities required and the effects of different amounts on the transition temperature between calcite and aragonite.

FACTORS AFFECTING ACCURACY OF PALEOTEMPERATURE METHOD

Several factors may influence the accuracy of the speleothem method of paleotemperature determination. They can be divided into two groups: those affecting the temperature of formation of calcite and aragonite, and those concerning the deviation of cave temperature from actual average annual temperature.

The effect of changing amounts of other ions on the temperature of formation of the two polymorphs of calcium carbonate is believed to be the principal possible source of error in this method. Because unstable aragonite occurs in caves in limestone of several ages and in regions that have had different tectonic histories, it seems unlikely that the trace-metal content of solutions entering these widely spaced caves could have changed so uniformly as to cause the deposition of aragonite in a belt as shown in figure 1.

Organisms such as bacteria and algae have been reported in caves (Magdeburg, 1933) and could possibly alter the conditions under which calcite and aragonite are deposited and thus introduce errors into the method. Also one mineral might serve as a nucleus, causing that crystal form to continue to be precipitated even after the proper temperature conditions no longer prevail (Murray, 1954, p. 488).

Caves at the same latitude and altitude may have slightly different temperatures depending on their humidity. Dry caves are warmer than wet ones. All the caves studied in this investigation have about 100 percent relative humidity; if in the past some were dry, an error could be introduced into the temperature calculation. Another source of error is thermal lag in caves (Lange, 1954). Because of the slow rate of flow of heat through rock, temperatures of caves may lag to a measurable extent behind the thermal conditions of the surface. Hot springs also could alter the temperature of certain caves.

In spite of these factors which could influence the accuracy of the method of paleotemperature determination, the evidence for a warmer climate in the past is still not removed. The agreement of data over a broad area may preclude the possibility that local factors had much effect.

CONCLUSIONS

The calcium-carbonate geologic thermometer allows an interpretation of the past temperature of western United States. It shows that the temperature was warmer several thousand years ago than it is today and suggests that during the Thermal Maximum the average annual temperature was about 15°F warmer than at present.

This method of paleotemperature determination might find application to other problems. Possibly it could be used to determine the temperature of formation of some epithermal ore deposits. Although much work is needed to evaluate the exact role of trace amounts of large cations and of organisms

on the transition point between calcite and aragonite, the calcium-carbonate method may at least provide a qualitative measure of past temperature.

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THERMAL CONDUCTIVITY IN THE DEPTHS OF THE EARTH

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ABSTRACT. If temperatures in the interior of the Earth are well above a low red heat, it is probable that radiative transmission rather than ordinary thermal conductivity becomes the dominant factor in heat-transfer. This should have the effect of reducing temperature gradients and temperatures in the interior, as compared with estimates based on the ordinary conductivity.

In the uppermost two or three kilometers of the Earth's crust, it is known by direct observation that the temperature increases with depth. Spicer (1942) lists the experimental facts for several hundred wells and mines, but only nine of these relate to depths as great as 2 kilometers and none attain 3 kilometers. Since that date (1942) a modest number of deeper wells have been logged, but it is still true that we have next to no information at 4 kilometers or more. There has been much speculation and calculation as to the cause of the heat flow and as to the temperatures at greater depths. Earlier generations attributed the temperature rise to primeval fires and molten rock in the Earth's interior, but with the discovery of radioactivity it became clear that relatively superficial layers of rock could account for the whole of the heat flow. Birch (1954) suggests that at a depth of 30 kilometers the temperature may be somewhere between 300°C and 680°C rather than the 900-1000°C envisaged by Daly (1933). The purpose of the present paper is to call attention to the fact that whereas at 300°C, and lower, the conductivity of silicate materials is essentially of the kind we know at "room" temperatures, at 680°C a new mechanism is becoming significant, and at 1000°C or higher it may be very important. This is "radiative transmission," which acts like an enormous increase in thermal conductivity, and its effect could be to reduce thermal gradients to very low values. Thus the whole of the deep interior of the Earth might be at a much more uniform temperature, and a much more modest temperature, than estimates based on the "ordinary" thermal conductivity would lead us to expect.

The matter has not entirely escaped notice in geophysical literature. Thus Birch and Clark (1940) in a massive, two-part paper dealing almost entirely with the "ordinary" thermal conductivity of many minerals and rocks, and some glasses, in the temperature range from 0 to 200°C, with some observations on minerals up to 350°C or even 400°C and, in the case of glasses, 500°C, have two well buried notes showing an awareness of the possibilities of radiative transfer. At the foot of page 541 they discuss the possibility that some of the heat in their apparatus may be passing through the specimen in a single jump, from their heater to their receiving plate, and on page 542 they conclude, no doubt correctly, that *below 300°C* this effect is probably negligible. Then they add the significant *caveat*: "In a vitreous shell deep in the Earth, at high temperatures, radiation might play an important part in the transfer of heat; its effect seems to have been little studied for such a system." (I may add here that it is not obvious that the shell has to be *vitreous*, and in fact the requirement seems most unlikely to be important, so that the

more commonly held view that the "shells" at depth are most likely crystalline, and not vitreous, would not affect the argument.)

Again on page 553, Birch and Clark, commenting on the rising conductivity of glasses, including Obsidian and artificial Diabase, with rising temperature, say "the upward curvature of the conductivity of silica glass and pyrex glass may be the result of radiative transfer of heat, which, as we have seen, may become important for the glasses above 300°C."

The present paper then may be regarded as an extension of remarks on the two quotations given above, calling attention to recent relevant investigations on artificial magmas of more than laboratory size, that is, upon molten glass in industrial furnaces or "tanks."

In glass-melting furnaces it has been known for several decades that the apparent or "fictive" conductivity is enormously greater than the "true" or "ordinary" conductivity, a point demonstrated by McCauley (1925). Although the present writer originally but erroneously ascribed this to mass transfer of heat by convection and circulating currents (Preston, 1936), he began to suspect that it was really due largely to radiative transfer (Preston, 1947). McCauley shows that the "effective conductivity" of the commercial glass he was investigating rises from about 20 BTU per square foot per hour per degree Fahrenheit per inch at 1000°F. to about 680 BTU at 2400°F. This is a rise from 0.007 calories/cm sec°C at 550°C to 0.238 at 1320°C.

Kellett (1952a, 1952b) solved the theoretical problem in a simple manner, showing that the "radiation conductivity" is $8\sigma\theta^3/\alpha$ where σ is the Stefan-Boltzmann constant, θ is the absolute temperature, and α is the absorption coefficient of the glass. The "thermal conductivity" in this sense, then, is not so much a property of the material as of the absolute temperature, and it varies as the cube of that temperature. For ordinary sheet glass, a soda-lime-silica glass, he concludes that the radiation conductivity at 1200°C is about 0.117 cal/cm sec°C, and that this is about 50 times the ordinary thermal conductivity. He points out that because the radiation conductivity varies as the cube of the absolute temperature, it is ineffective at temperatures below about 500°C, where it is "about 0.0014 cal/cm sec°C, which is only about two-thirds of the ordinary thermal conductivity."

We may note in passing that his estimate of the ordinary thermal conductivity is in fair agreement with the values of Birch and Clark, who find that for a large number of minerals, rocks, and glasses at room temperature the ordinary conductivity lies generally in the range from 3 to 14 x 10^{-3} cal/cm sec°C, i.e., from 1½ to 7 times Kellett's estimate.

The radiative conductivity of industrial glasses, and no doubt of the "shells" of the Earth, varies greatly with the absorption coefficient, which is largely a function of the iron oxide content. Kellett estimates that for a glass containing 0.8 percent of iron oxide, the radiation conductivity at 1200°C is about 0.006, i.e., about 1/20 that for glass of sheet glass composition, and only about three times the ordinary thermal conductivity. However, even a three-fold increase in conductivity is quite significant, and at 1500°C the increase would be six-fold.

It may be proper to comment here that Kellett does not define his "iron oxide" more precisely, and that the absorption coefficient is greatly affected by the state of oxidation of the iron. to use the older terminology. Ferrous oxide in silicate glass absorbs strongly in the near infrared, though Merren (1951) has shown that such glasses are more diathermanous when hot than when cold. Ferric oxide absorbs much less in the infrared, and iron sulphide not at all. This may have some relevance to the properties of the Earth's shells at depth.

For a review of the work of Czerny and his school at the University of Frankfurt, Germany, on radiative transmission in glasses, see Eitel (1955).

So far as the interior of the Earth is concerned, the relevance of the work on molten industrial glasses may be limited by several factors. One we have just mentioned—the uncertainty as to the content of iron in the various shells, and the form of that iron. Another is the great uncertainty as to what the actual temperatures are at any depth beyond the first few kilometers, where radiative transmission is ineffective anyway because temperatures are strictly modest. Still another problem is posed by the possibility that the shells are largely crystalline, with many grain boundaries. These tend to reduce the mean free path of the radiation and thus reduce the effective conductivity. Some theoretical work has been done on this by Condon (unpublished). It is important in understanding the behavior of the refractories that are used to contain the molten glass. However, it is well known that modern electrocast refractories consisting of crystals of corundum and mullite with some interstitial high-silica glass behave as though they had a much higher thermal conductivity than the old-style, fine-grained metakaolin refractories, commonly called clay blocks, and in view of the experimental results of Birch and Clark, who show that most minerals have rather comparable ordinary thermal conductivities, this may perhaps be tentatively ascribed to a higher effective conductivity arising from greater radiative transmission. It seems likely that in the depths of the Earth the materials would much more resemble electrocast refractories than they would clay blocks, and in fact would have an even higher conductivity unless the content of iron (and perhaps chromium and a few other elements) in the Earth becomes the controlling factor.

I should like to acknowledge the usefulness of comments from Dr. L. H. Adams and Professor Francis Birch in the preparation of this memorandum.

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CONCENTRATION OF BRINES AND DEPOSITION OF SALTS FROM SEA WATER UNDER FRIGID CONDITIONS: DISCUSSION

GEORGE W. BAIN

The article by Thompson and Nelson in this Journal (April, 1956) represents careful and detailed laboratory study of the behavior of sea water at the lowest temperature attained in a marine environment. However, it is neither correlated with nor illustrated by cases from nature. Before these data are used to explain a record in strata, the environment of a salt deposit made during the past should be examined to determine whether it too bears evidence of (a) having had a physical connection with the sea, (b) having been at the lowered temperatures necessary to produce these salt concentrations. Application of experimental work to a natural environment requires that the experiment satisfy all aspects of a problem rather than the physico-chemical aspect alone. Testing lowered temperature, as a cause for salt concentration adequate to have *caused* salt deposition or to have influenced locus of deposition, can be divided into two categories; the first relates to formation of alkali sulphates, the second concerns the environment for the chlorides. All the laboratory results are accepted as accurate; the only test used here is "do they apply to any known deposit." Having been involved deeply in study of paleoclimates (Bain, 1953), this subject is not new to me.

David and Mawson report mirabilite in the ice-covered lakes of Antarctica; calcite crystals pseudomorphous after glauberite, called glendonites, occur in many shales around the Permian age glacial deposits of Tasmania and New South Wales. These are single crystals and none form even discontinuous strata. The sedimentary rocks around the two Permian glacial centers, one in Africa south of the equator and the other in eastern Australia, have no salt deposits of any kind. However, mapping these two ice cap areas as near-polar on a globe, as were the ice caps of the Pleistocene, serves to locate the known Permian salt areas of the world, including the Gran Chaco (S.A.), mid-continent (N.A.), Brunswick-Stassfurt-Salzburg and Perm (Eur.) not only very distant thereto, but symmetrical and adjacent to an equatorial zone. The scattered glendonites of southeastern Australia represent the only known occurrences of alkali sulphate minerals associated with polar climate deposits. The paucity of known occurrences is not due to lack of search.

The alkali lakes of western North America, Siberia, Australia, and Africa south of the equator did not come into existence until the sea had receded from the region. Not a single one owes its form to sea floor irregularity; origin of their basins varies from wind scour to block faulting, but nowhere is the topographic floor of the basin any part of the sea floor. Analyses of the lake water, and minerals precipitated from the brine, vary from basin to basin and generally are related to the soil components in the local interior drainage.

This is particularly outstanding in the nitrate salars of Chile which were derived from the Pliocene-age chernozems.

Salt lake deposits of the past are illustrated by occurrences in the Triassic basins of eastern North America. Both salt and glauberite pseudomorphs are known and water samples with chlorinity exceeding 1500 parts per million have been taken at Westfield and Gill, Massachusetts. Frost crystal casts occur on the reptile footprint slabs, but the biotic associations indicate intermittent desert cold rather than perennial polar cold.

The chloride and lime sulphate compounds make the most extensive salt deposits. Listing of a few outstanding ones and considering their entire environment will show that none had a sustained temperature approximating the freezing point of even pure water. The salt deposits encountered under the Bitter Lakes along the Suez Canal represent the most recent extensive salt deposit and they formed in the low latitude edge of a Mediterranean climate. The strata associated with Oligocene age gypsum and salt of the Mulhausen, Paris Basin, Barcelona, and Egyptian regions have a mammal population density and type which is non-polar but is typical of the low latitude part of a Mediterranean climate. This is confirmed by the marine invertebrates of the Eocene strata below and of the Miocene age beds above. The next older extensive salt deposits are the Jurassic strata of the Gulf of Mexico area and the deep part of the Artesian Basin of central Australia. The Gulf area salt deposits are flanked by the Navajo aeolian sandstone in the west and by laterites indicated by detrital bauxite in the lower Cretaceous of Arkansas. The Jurassic age salt deposits of Australia do not outcrop, but the strata, which do, have reptilian remains. The Permo-Trias of Morocco and the Triassic of Szechwan are small and not well known but both are in red beds which are essentially strangers to Polar area sediments. It is hardly necessary to dwell upon the warm water fusuline and coraline faunas of beds associated with the mid-continent Permian basin or that of Europe and the U.S.S.R. The areally extensive (not linear extensive) dune deposits, which make the Coconino and de Chelly sandstones, tell of trade wind deserts rather than polar climates. The Mississippian age salt beds of the Maritime Provinces of Canada are associated with warm water faunas whose polyps drifted in from North Europe, indicating a near equatorial drift position during that time because coral and brachiopod polyps migrate only with the current. The Salina beds of the Silurian System extend intermittently from the Appalachians to the Mackenzie River delta and from Indiana to Hudson's Bay. The fauna associated with beds below and above is a warm water type; dune deposits in the overlying strata in the Great Lakes region, mudcracks of a desiccation rather than frost-rifting type, and dune deposits in Gotland suggest trade wind desert rather than polar concentration of salt.

Thompson and Nelson give a scientifically valid process for producing salt concentrations. Applying this process to regions with known alkali sulphate, carbonate, and nitrate deposits and to the regions of lime sulphate and

alkali chloride deposits demands existence of a series of contemporary geomorphic and sedimentary features which are not found with the one exception of the glendonites of eastern Australia. On the other hand, examination of the known salt deposits of the world show that the associated alkali sulphate centers are just peripheral to the continental monsoon centers, and that the chloride and lime sulphate deposits lie in a desiccation belt between the subequatorial high pressure zones and the equatorial low pressure belt for their respective ages.

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REVIEWS

Niels Bohr and the Development of Physics; edited by W. PAULI, L. ROSENFELD, and V. WEISSKOPF. P. vii, 195. New York, 1955 (McGraw-Hill Book Company, $4.50).—This is a commemorative volume published on the occasion of Bohr's seventieth birthday. Contributors are Bohr's associates and friends, both old and new.

C. G. Darwin describes what might be called the prehistory of the modern atom and leads up to the earliest of Bohr's discoveries. Next, Heisenberg, in a remarkable survey article, reviews various modern interpretations of quantum mechanics and concludes with one of the most penetrating statements of his own position with respect to the meaning of measurement in the physical microcosm. The exclusion principle is discussed by Pauli in connection with some modern ideas concerning the reflection of space-time and charge; his paper is readable only by experts in the field, but even its awkward style and strange philosophic terminology cannot hide the brilliance of mathematical conception and the analytic thoroughness that characterize Pauli's writings.

A very readable and well composed article on the quantum theory of fields is Landau's contribution. The same theme is continued by Rosenfeld and Klein. The latter author deals in illuminating fashion with the problems which arise from the fusion of quantum theory and relativity. The remaining four articles are topical in nature and treat special problems of modern physics to the solution of which Bohr made important contributions. Casimir presents the theory of superconductivity; Friedman and Weisskopf give a useful and interesting simple picture of the compound nucleus. Wheeler, who was associated with Bohr in the epoch-making work which led to a theoretical understanding of fission, treats nuclear fission and nuclear stability. The book closes with an article by Lindhard on the present status of theories explaining the passage of charged particles through matter.

As would be expected, the treatment of topics in the book is quite uneven. While there is no observable endeavor to please the reader, the practice of several contributors to tell charming anecdotes about Bohr and his associates makes the perusal of this little volume a delight even for those whose interest in the development of modern physics is only historical.

HENRY MARGENAU

Transactions of the International Astronomical Union, v. 8; edited by P. TH. OOSTERHOFF. P. x, 888. Cambridge, 1954 (Cambridge University Press, $10.50).—The triennial meetings of the International Astronomical Union had as their original function the reports, discussions, and resolutions of the various commissions. While these continue to be a prime purpose, they are gradually being supplemented by large symposia. Published results of the meetings bulk larger each session with growth of the Union and the added symposium functions.

The present report covers the eighth meeting, held at Rome in September, 1952. There are the traditional 50 pages of preliminaries and 25 pages of resolutions of committees. But for the general reader the important material follows in Part III, which contains more than 500 pages of commission reports

wherein the respective chairmen sum up the important work done in their fields since the previous meeting, and in which the actual committee sessions are reported in detail. Among a host of important contributions, the historic report of Baade establishing the revised distance scales to external galaxies perhaps stands out. The last several hundred pages are devoted to the four symposia on Stellar evolution. Astronomical instrumentation, Problems of astrometry of faint stars, and Spectra of variable stars. With very few exceptions the contributed papers are of the high standard expected of an international meeting.

For a bird's-eye view of astronomy in 1949-1952 this volume is indispensable. The main difficulty with such massive publications lies in the necessarily long time required to assemble and publish them. Thus this one appeared less than a year before the subsequent meetings in September 1955 at Dublin. Considering the awkward size of the present volume in addition to the publishing delay, it may soon become necessary to print the symposia separately.

HARLAN J. SMITH

Les Dislocations et la Croissance des Cristaux; by W. DEKEYSER and S. AMELINCKX. P. viii, 186; 80 figs., 57 photographs in 23 pls. Paris, 1955 (Masson et Cie., 2000 francs).

Crystal Growth and Dislocations; by A. R. VERMA. P. xii, 182; 76 figs. including 48 photographs. New York, 1953 (Academic Press, $5.00), London (Butterworth's Scientific Publications).

Early theoretical studies suggested that perfect crystals ought to have much greater tensile and shear strengths than are actually observed, and more recent theory shows that the growth of a truly perfect crystal is virtually impossible because of a high energy barrier that tends to prevent nucleation. The edge-dislocation, defined in 1934 by several authors working independently, can so localize stresses that failure in shear or tension is easily explained, but cannot account for the rapid condensation of material on a growing crystal in a medium having only a slight degree of supersaturation for the depositing material. The screw-dislocation, defined by Burgers in 1939, and considered at length in these two books, not only accounts for rapid growth by affording a self-perpetuating nucleus but also solves the problem of the astonishingly complex patterns of stacking of simple sheet-like units that are found in SiC, wurtzite, micas, and other crystals showing extensive polytypism. This subject is mentioned by Verma but is developed more fully by Dekeyser and Amelinckx.

Differences in emphasis on the part of Verma on one hand, and Dekeyser and Amelinckx on the other, account for most of the differences between these books. Both books are concerned with an overall summary of the subject, and each in its own way serves well the purpose thus defined. Verma is generally more rigorous and precise in his descriptions and mathematical formulations; he gives more complete derivations of the equations and the theories with which they are concerned. Dekeyser and Amelinckx, on the other hand, are more concerned with furnishing examples of the same ideas and consequently have used more drawings and photographs. Verma's choice of only the best

available illustrations to illustrate his ideas is, however, highly commendable. Both books have drawn heavily on published photomicrographs and electron micrographs, so that some of the same ones are used in both. Verma practically always gives magnification and other details on each illustration (as phase-contrast microscope, polarized light, reflected or transmitted light, electron micrograph of replica or of replica with evaporated metal film, etc.), whereas Dekeyser and Amelinckx frequently omit this information. Verma's chapter on procedures is somewhat longer, and to this reviewer rather clearer; Dekeyser and Amelinckx's chapters on polytypism, on corrosion figures, and on growth of hopper- or funnel-shaped crystals are much more complete. It seems odd to find in the later book (Dekeyser and Amelinckx) no reference to the earlier one, although there are references to articles by Verma published both earlier and later than his book.

In a case where two books are as similar as these, perhaps a choice of one over the other will be made in the long run on the basis of the accessory aids furnished the reader to enable him to refer to specific subjects without having to re-read the entire book. In this respect a rather common complaint about inadequate indexing of French books in general is well exemplified; the contrast strongly favors the English one: we find in Verma's work an excellent subject index (300 items), a complete table of contents (70 items), and a conveniently arranged bibliography (210 articles by about 100 authors). Dekeyser and Amelinckx's table of contents has 14 items, there is no subject index, and the index to about 150 authors' names gives page references to the text citations that refer in turn to serially numbered bibliographies at the ends of the several chapters. Perhaps preventing scholars from reading parts of a book out of context may have advantages, if it can be assumed that the scholars will actually read the whole book. In the present instance, the reviewer prefers Verma's book for future reference but feels well rewarded for having read both books carefully. HORACE WINCHELL

Arctic Research; edited by DIANA ROWLEY. P. 261; 28 figs. Special Publication No. 2 of the Arctic Institute of North America (reprinted from *Arctic*, v. 7, nos. 3 and 4, p. 113-366). Montreal, 1955 ($3.50).—The current status of research and some of the immediate problems in the North American Arctic and Subarctic are summarized in this symposium. Leading investigators in all fields of science have contributed to this volume; extensive bibliographies are included with over half of the 27 papers.

The physical sciences are discussed in 12 papers. The history, use, and present status of meteorological activities in the Canadian Arctic are analyzed by R. W. Rae. The state of knowlege and unsolved problems associated with arctic geology and geomorphology are discussed by J. C. Reed and H. S. Bostock, and P. D. Baird and R. P. Sharp have reviewed the background and some of the areas that appear worthy of further investigation in glaciology. Potential fields of research in the study of permafrost are outlined by R. F. Leggett. Geophysical activities in Alaska and Canada are briefly described by L. O. Colbert, H. R. Joesting, J. E. R. Ross, and others in a series of separate papers which encompass almost all aspects of applied geophysics.

The pressing need for further study of the ionosphere over northern Canada in order to understand short-wave radio interference is emphasized by F. T. Davies. Oceanic circulation, tidal conditions, and sea ice receive consideration in separate papers by C. O'D. Iselin, L. O. Colbert, and Terence Armstrong.

A total of 9 papers concern the biological sciences. Problems encountered in limnology, marine ecology, and botany in the Arctic are independently reviewed by D. S. Rawson, M. J. Dunbar, and H. M. Raup, respectively. Arctic soils and agriculture are outlined by A. H. Mick, and H. A. Johnson for Alaska and A. Leahey for Canada. Additional biological papers include discussion of the current status of knowledge concerning arctic vertebrates and invertebrates.

A total of 5 papers are devoted to the social sciences. H. B. Collins has sketched out the situation of archeological research in the North American Arctic. Human ecology and geography are outlined, and the associated problems of settlement and transportation are discussed in the concluding papers.

Arctic work often requires close association of scientists from a wide variety of fields; each man must be familiar with some of the problems facing the other members of the team. For this reason, this book would be a useful addition to the library of anyone engaged in, or contemplating, arctic research.

DONALD G. MACVICAR, JR.

Vocabulaire Franco-Anglo-Allemand de Géomorphologie; by HENRI BAULIG. P. xiv, 230. Publications de la Faculté des Lettres de l'Université de Strasbourg, v. 130. Paris, 1956 (Les Belles Lettres, 800 francs).—Professor Baulig has competently rendered a very useful service in compiling this vocabulary of synonyms and near-synonyms of terms in geomorphology in English, French, and German. A rough calculation indicates that around 8000 terms (including all three languages) are dealt with.

In the body of the book the terms are grouped mainly according to process, so that their organization is much like that of a textbook of geomorphology. A typical entry is: soil-creep / creep, reptation / Kriechen, Gekriech; this is preceded or followed by a definition, either direct or by implication. As there is an index listing every term used, regardless of language, the arrangement by process is not a disadvantage to the use of the book as a dictionary.

The coverage is quite good, and the work is preceded by a thoughtful introduction on the formation of morphologic terms. This is worth a reading even by those who have no need for the vocabulary.

RICHARD FOSTER FLINT

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